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Fourth Conference on Advanced Pollution Control for the Metal Finishing Industry Presented at Dutch Inn, Lake Buena Vista Florida - January 18-20, 1982

American Electroplaters' Society, Inc.
Winter Park, FL

Prepared for

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The "Fourth Conference on Advanced Pollution Control for the Metal Finishing Industry" was held in Lake Buena Vista, Flordia, January 18-20, 1982. This broad-scoped colloquium was jointly designed by the American Electroplaters' Society and the U.S. Environmental Protection Agency's Nonferrous Metals and Minerlas Branch. The primary objective of this Conference was to continue the dialoque established at the First EPA/AES Conference (1978) and strengthened at the Second and Third EPA/AES Conference (1979 and 1980), respectively) between key members of the EPA and the metal finishing industry. The proceedings of this Fourth Conference reflect the primary points of the gathering: the status of EPA's wastewater and solid waste regulations, and both EPA's and industry's efforts to effectively address the ramifications of these regulations. Special sessions of the conference were devoted to metal finishing solid waste, practical pollution control alternatives, recovery technology, emerging technologies, and innovative alternatives. The proceedings contain twenty papers reporting on this work.

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Fourth Conference On Advanced Pollution Control For the Metal Finishing Industry

PRESENTED AT:
Dutch Inn, Lake Buena Vista, FL
January 18-20, 1982

Co-sponsored by:
- The American Electroplaters' Society
- The United States Environmental Protection Agency

Industrial Environmental Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, OH 45268

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Notice

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Foreword

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory-Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

These proceedings cover the presentations from the "Fourth EPA/AES Conference on Advanced Pollution Control for the Metal Finishing Industry." The purpose of the conference was to inform industry on the range and scope of research efforts underway by EPA and others to solve the pressing pollution problems of the metal finishing industry. It is hoped that the content of these proceedings will stimulate action to reduce pollution by illustrating approaches and techniques high-lighted by the wealth of excellent papers presented at this conference. Further information on these projects and other metal finishing pollution research can be obtained from the Nonferrous Metals and Minerals Branch, IERL-Ci.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

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Introduction

"The Fourth EPA/AES Conference on Advanced Pollution Control for the Metal Finishing Industry" was held in Lake Buena Vista, Florida on January 18-20, 1982. This broad scoped colloquium was jointly designed by the American Electroplaters' Society and the U.S. Environmental Protection Agency's Nonferrous Metals and Minerals Branch. The primary objective of this conference was to continue the dialogue established at the First EPA/AES Conference (1978) and strengthened at the Second and Third EPA/AES Conferences (1979 and 1980, respectively) between key members of the EPA and the metal finishing industry. The proceedings, contained herein, of this Fourth Conference reflect the primary points of the gathering: the status of EPA's wastewater and solid waste regulations, and both EPA's and industry's efforts to effectively address the ramifications of these regulations. Special sessions of the conference were devoted to metal finishing solid waste, practical pollution control alternatives, recovery technology, and emerging technologies and innovative alternatives; reports of this work appear in these proceedings.

The program of the conference was broken into six segments: wastewater and solid waste regulatory status; solid waste, regulatory overview and research; practical pollution control alternatives, focusing on air, water, and solid waste pollution control solutions; recovery emphasizing research progress and field application results of wastewater recovery technology; an open forum discussion between members of the government and industry on regulatory reform; and a session on emerging technologies and innovative alternatives which highlighted several approaches such as centralized waste treatment. Since attendees at the first, second, and third conferences placed extreme emphasis on wastewater and solid waste, the first segment of the Fourth Conference was structured to provide conference attendees with a detailed understanding of the potential impact of current and future regulations in these two important environmental areas. Key EPA officials, representing EPA's water and solid waste regulatory offices, described the procedures by which EPA prepares and promulgates regulations having a direct impact on metal finishers.

The second segment, entitled "Solid Waste," provided the conference attendees with an overview of the solid waste regulations and the delisting procedure. Descriptions of technical and administrative difficulties and solutions for metal finishing solid waste were also presented.

Since numerous industrial plants are currently attempting to comply with various air, water, and solid waste regulations, the third and fourth segments of the conference discussed practical current solutions to major pollution problems. A majority of the presentations from these two segments were given by industrial participants who are faced with the burden of regulatory compliance. The latter segment focused on recovery technology for metal finishing wastewater.

The fifth segment, entitled "Regulatory Reform - An Open Forum Discussion" was conducted during an evening session. Panel members representing EPA, industry, and the Natural Resources Defense Council individually provided opening remarks focused at regulatory reform. The panel then opened the floor to a free discussion in order to permit all attendees to commonly and openly discuss the topical subject as well as other related environmental concerns.

"Emerging Technologies and Innovative Alternatives" was the title of the final segment. Presentations described new developments that could eventually solve key environmental problems. One alternative to conventional single plant treatment, namely centralized waste treatment, was described both technically and administratively.

This conference, attended by more than 400 persons interested in the environmental problems faced by metal finishers, was considered an extraordinary success. The principal purpose of the conference, to continue a fruitful dialogue between industry and EPA, was achieved. The high-priority research needs of the industry were identified and solutions to pressing problems are being sought—some jointly—by EPA and AES.

The proceedings are published here in order that the important material presented at the conference can benefit as many people as possible interested in solving the intricate problems inherent in metal finishing processes. These proceedings contain the presentations made by representatives of various EPA regulatory groups affecting the metal finishing industry, as well as presentations by parties actively addressing research and development in this same industrial area.

The EPA and the AES are pleased to have cooperated in this mutual endeavor which has improved communications and which should foster continued research resulting in sound technical solutions to the environmental problems of metal finishers.

George S. Thompson Jr.

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EPA Welcome to the Fourth Conference On Advanced Pollution Control For the Metal Finishing Industry

George S. Thompson, Jr.*

On behalf of the U.S. Environmental Protection Agency, I cordially welcome you to this Fourth EPA/AES Conference on Advanced Pollution Control for the Metal Finishing Industry. For many of you, this may be the first EPA/AES conference that you have attended; for some of you, hopefully this is your fourth. This conference has been structured so that while you listen and participate, your (and our) gain in knowledge on today's environmental issues will prove its worth in conducting your daily business activities.

Looking back to last December, while sitting in my car stranded in a midwest snow storm knowing that I would be late for work, I took the opportunity to structure my "welcoming address" thoughts to you. Obviously my initial thoughts centered around Florida's January climate. I consider this climatic advantage to be just a small incentive in getting you here; the real incentive continues from our First EPA/AES Conference in January 1978. We will, as a unified group, discuss our mutual environmental problems through open forum format. We will provide the latest information on regulatory actions that affect your metal finishing operations. We will also mutually share our knowledge on research efforts and proven solutions to some of our most pressing air, water, and solid waste concerns. We have also modified our evening session; it will address a topic of interest to each and everyone of us—Regulatory Reform. I solicit your active participation for the next three days. I wholeheartedly request that you not only listen, but also constructively comment and provide the wisdom that only you from industry possess.

I will take this opportunity to offer EPA's special thanks to Harry Litsch, Howard Schumacher, Fred Steward, and numerous other AES members for their continued interest in open discussion and joint solution of our environmental problems. I quote the following which was provided by Mack Truck's Chairman of the Board, Mr. A. W. Pelletier, as part of his introductory remarks at our December 1981 VOC Seminar in Allentown, PA.

> "So much publicity today focuses on business and government as adversaries, that we sometimes overlook the real progress possible when we both work together. . . . Communication and cooperation must be our guidewords for the future, because our national and international economic strength depends on it now more than ever."

With these statements in mind, I officially welcome you to our Fourth Conference. Let us continue to actively and effectively communicate and cooperate.

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Keynote Address

Bruce Barrett*

I want to commend the leadership of the American Electroplaters' Society, George Thompson of EPA and consultant Bob Schaffer of CENTEC Corp. for their leadership in developing this 4th Conference on Advance Pollution Control Techniques.

We all know there have been many environmental problems associated with regulation of this industry, and if we continue to meet and discuss the problems, have a good healthy debate of the issues, and continue talking to each other, we will solve these problems. We're getting closer all the time.

The metal finishing industry is one of the most environmentally conscious of all industries. This is evident by the outstanding turnout we have in this room today. I understand that there are over 400 people here.

This morning I want to discuss some of the policies and goals of the new Administration in EPA; some of the regulatory issues that are of specific interest to the audience, such as pretreatment; then close with a brief discussion of where we are on the Clean Water Act amendments that will be coming up in the coming weeks and months.

Administrator Anne Gorsuch, when she came into office last year, set forth a number of priorities for the Agency. I'm not going into all of them, but at the top of the list is to have good science; and to have a sound scientific underpinning of the regulatory programs that we're responsible for implementing under the Clean Water Act. One of the problems that EPA had in the past was that the science was inadequate. Consequently, we would promulgate a regulation, promptly find ourselves in court, and more often than not come out on the short end of that litigation. There has been a lot of wheel spinning. We now intend to instill good scientific underpinning to our regulatory programs. In the beginning this may add a little lead time; however, in the long run it's going to be quicker and better for all parties concerned. We have a new peer review system that is going to guarantee that we get better science into our regulations.

The Administrator also wants to emphasize delegating more water pollution programs to the State Agencies. In the past some of the procedures we've established have been excessive. We want to do everything we can to get more programs delegated to the States.

We're now considering some new compliance monitoring strategies in our enforcement program that we think will significantly improve our enforcement program. In the past our inspection coverage would plow an inch wide and a mile deep. We would go into an industrial plant and take samples and inspect the facilities for compliance with their permit and spend as long as a week or ten days taking multiple samples. Consequently, we were not getting the kind of inspection coverage that a good, sound enforcement program needs, so we're going to be looking at changes in strategy that will provide broader coverage. Instead of an inch wide and a mile deep, maybe we'll go a mile wide and an inch deep and focus on more inspections of shorter duration. When we are faced with the possibility of litigation, we could go to the more extensive inspection trips. Another emphasis in the enforcement area is to provide more technical assistance to the operator. Instead of a completely adversarial process, we have to provide technical assistance and guidance to the plant operators when they want and need it.

We want to simplify and streamline the regulations generally. We want to eliminate unnecessary regulatory requirements that place an undue burden on State and local government and on the business community. The philosophy in the past has been: How much can we lawfully include in the regulations? We want to look at the flip side of that philosophy and say: What does the law require in the regulations, and add to that legal minimum only those additional requirements necessary to make the program operate smoothly and effectively.

As I mentioned earlier, regulatory requirements have discouraged, rather than encouraged, the States from assuming the lead role in water quality management. The need for regulatory reform is clear. We, both the regulators and the regulated, are choking on a procedural morass of regulations. Requirements are so burdensome and confusing as to be counter-productive.

Our nation's water pollution control effort has been tied up in red tape and plagued by uncertainty in a protracted adversarial process which confuses everyone. I'll give a couple of examples here. I'm sure most of you are familiar with our consolidated permit regulations. That was an idea, good in theory, but in practice just didn't work very well. It was one of those situations where the total package turned out to be more than the sum of the individual parts. Instead of a one-stop shopping place for a permit for our water, air, and solid waste programs, more confusion and regulatory requirements were added. The resulting package was 298 pages of fine print in the Federal Register. It would take a Philadelphia lawyer to understand the process. We're now revising the consolidated permit regulations and trying to simplify, cut back, and eliminate the extraneous material.

Another area we're looking at is the water quality standards regulations. We expect to have the proposal out on those regulations in the next few months. Water quality standards regulations are the foundation of any water quality management program. When in-stream water quality standards are established, the basis for the entire program is because they drive everything, particularly permit limits. We will include in the new package a use

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attainability analysis. In the past it was assumed that every stream, every river, and every lake would meet the statutory goal of fishable, swimmable waters. We now know that there are some streams which, because of various physical or environmental factors, will never be suitable for fishing or swimming.

Another feature we're adding to the water quality standards regulations is the benefit/cost assessment. What does it cost to attain the water uses that you're trying to attain? Do you want to spend that kind of money? We're going to have a process where the States can make an assessment of the cost and the benefits to be gained.

And finally, we're going to include site-specific criteria development. You've all heard of the red book, which is the water quality standards criteria document that until recently was presumably applicable to every stream in the country. We're developing a process now where those criteria can be modified to meet the requirements of a given stream. Not all streams have the same biological characteristics. There are different fish, different aquatic plants, different organisms. The end product will be the development of State water quality standards that are more realistic and more attainable.

As I mentioned earlier, we've all known for a long time of the dilemma faced by environmental control of the metal finishing industry. Your industry is characterized by a lot of small firms dealing with many toxic wastes. It has been a serious problem. Several years ago, a very high closure rate was predicted for the industry. As I recall now, they were talking in terms of a 50-percent closure rate for the electroplating industry. I think we're now seeing some light at the end of the tunnel.

We are now considering strategies we hope will achieve the environmental protection needed while greatly reducing the cost of compliance. The Agency is now involved in a major effort to review the entire pretreatment program. We're examining a range of options that includes everything from the existing program to applying it only to selected industries, or to selected pollutants utilizing specific technology, or to water quality based effluent limits on publicly owned treatment works as a means of control using pretreatment to address only documented problems. Whatever program we develop in pretreatment, it is absolutely essential to have the support of local government. Federal and State agencies do not have the resources to adequately control the thousands of indirect dischargers into municipal sewage treatment plants. Only local government has that capability. Whatever program we develop is going to have to accommodate that fact. The program that we've been trying to sell is too complex—it just hasn't gotten the job done.

My personal view on pretreatment is that we should maintain the general pretreatment standards that prohibit the discharge of flammable materials, explosives, materials that attack the structural integrity of sewage treatment plants and sewer systems generally, and materials that interfere with the operation of the plant. Local government would then establish the pretreatment program as needed to comply with the terms of their own permit or to protect the quality of the sludge. The categorical pretreatment guidance would then be available to the cities to use as necessary to require whatever pretreatment they would need to protect their own investment and meet the terms of their permit.

Some of these approaches are probably going to require legislation. We need to examine what can be accomplished within the framework of existing law and what legislative changes may be required to come up with a workable program.

I might mention that we had a contractor's report out for comment and review about a month ago which examined this whole range of options, and I sincerely hope that the AES and other industry groups will review that report and provide us with the benefit of their views on the pretreatment programs. No one has a bigger stake in that than this industry.

Touching briefly on removal credits—back in 1977, Congress amended the law to provide that where publicly owned treatment works were removing toxic wastes incidental to their normal function of removing the biological materials and solids, credit could be extended to their industrial customers that were discharging toxic pollutants. The problem was that the way the law was implemented was rather complicated, administratively burdensome, and required a lot of costly sampling and analysis. Because of that a lot of cities indicated they did not intend to grant the removal credits, which frustrated the intent of Congress in establishing them in the first place. We're working on a revision now that will simplify the removal credit mechanism by establishing national removal credits based on a study of some 40 publicly owned treatment works that was recently conducted by EPA. Cities meeting minimal performance criteria will be able to grant these credits without the extensive sampling and analysis and application procedures currently required. This should allow widespread use of removal credits. The credit could provide a significant cost savings for regulated industries. In the case of electroplaters, it will allow some facilities to comply with their adjusted categorical limitation through improved operation and maintenance, thereby eliminating the need for installation of pollution control technology.

I had the opportunity to review an editorial written by Fred Steward in the December Journal of the AES. I thought it was excellent. It dealt with the extension of the compliance deadline for electroplating effluent guidelines. Fred suggested that extension of time ought to be used productively by looking at recovery systems, treatment systems, and plans for sludge disposal. I want to say that I can second everything that he had to say in that well written and thought-out editorial.

Let me now shift briefly to the Clean Water Act and some potential amendments. We think the Clean Water Act is basically a very good law. There have been a lot of problems with the way the law has been implemented in the past but we believe that most of these problems can be rectified by regulatory changes—some of which I have just discussed—and by a lot of administrative changes. Probably 95 percent of the problems that we've had in the past with the Act can thus be rectified. There are three or four areas that we think may require legislative fixes. The first and most obvious, I think, is in the pretreatment area. As I mentioned earlier, we're looking at a range of options. Some of these may well require a legislative fix, and I think we'll be asking Congress to give us more flexibility in the law as it relates to pretreatment. Before I go on, let me hasten to add that the changes we are examining are preliminary and no final decisions have been made at this point.

Second, we're considering a water quality waiver to the BAT requirements. The thinking here is that if a discharger can show that the application of BAT over and above what he's already got in place would produce no discernible benefits to water quality, then perhaps he should not have to install additional treatment technology and incur the resulting costs.

Third, we're looking at the permit life for NPDES permits. As you know the current time for permits is five years. We think extending that to 10 years makes a lot of sense.

Lastly, the 1984 BAT compliance deadline looks pretty tough, if not impossible to meet! We may be asking Congress to extend that date. One method would be to extend it to three years after finalization of the BAT effluent guidelines. Another method would be to go to the 1988 date Congress just adopted last month for municipal dischargers.

That concludes my remarks. I hope you have a successful conference, and from my examination of the program I'm sure you will.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

Status of Effluent Guidelines for The Metal Finishing Industry and The General Pretreatment Regulations

Jeffery D. Denit*

As has been the situation in previous meetings, the regulations impacting the Metal Finishing Industry have not been finalized by the Agency. Also, as in the past, we are pleased to be able to be here to present the best information available and to allow you to have a preview of the Agency's thinking. The numbers I am about to give you and the options for implementing them are, at this point, only staff recommendations.

As these recommendations move through the Agency's approval process, it is possible that changes will be made before they are completed. You can, however, be fairly confident that the numbers presented will be very close to the final version. As Mr. Bruce Barrett said, we continue to strive for reasonable regulations and an open and cooperative regulatory process.

In developing the upcoming Metal Finishing regulations the Agency has responded to problem areas, and made modifications which will make these regulations clearer and more reasonable. The major changes in approach involve:

1. use of Concentration basis versus Production,
2. greater coverage of total plant process wastewater under one regulation,
3. consideration of removal which occurs at the POTW,* and
4. separation of job shops and printed circuit board manufacturers to account for economic impacts.

Each of the above will be discussed in detail followed by a presentation of the staff recommendations for the regulation.

I. Concentration versus Production

The Agency has examined a wide range of Production parameters to be used as the basis for regulation; floor area, power consumption, area operation, etc. All had problems, including:

1. difficulty in measuring area (i.e., one plant asked how to measure assorted buckets of screws),
2. flow variations depending on process, product quality, and process configuration (i.e., single stage rinse versus multistage countercurrent rinsing), and
3. enforcement authorities, particulary POTW's, finding product based regulations difficult.

II. Total Plant Coverage

The Electroplating regulation covered seven subcategories which tend to cover the total process discharge at job shops.

1. Electroplating of Common Metals
2. Electroplating of Precious Metals
3. Anodizing
4. Coating
5. Chemical Etching and Milling
6. Electroless Plating
7. Printed Circuit Board Manufacturing

However, approximately half of the captive facilities have significant wastes from other processes. This is particularly true in the automotive industry. These facilities generally combine wastes through one treatment system. To address requests from industry to regulate those facilities with one regulation reflecting combined treatment, the Metal Finishing regulatory category was developed. The Metal Finishing category has one subcategory and covers a broad array of processes, including the following list.

1. Electroplating
2. Electroless Plating
3. Anodizing
4. Conversion Coating
5. Etching (Chemical Milling)
6. Cleaning
7. Machining
8. Grinding
9. Polishing
10. Tumbling (Barrel Finishing)
11. Burnishing
12. Impact Deformation
13. Pressure Deformation
14. Shearing
15. Heat Treating
16. Thermal Cutting
17. Welding
18. Brazing
19. Soldering
20. Flame Spraying
21. Sand Blasting
22. Other Abrasive Jet Machining
23. Electric Discharge Machining
24. Electrochemical Machining
25. Electron Beam Machining
26. Laser Beam Machining
27. Plasma Arc Machining
28. Ultrasonic Machining
29. Sintering
30. Laminating
31. Hot Dip Coating
32. Sputtering
33. Vapor Plating
34. Thermal Infusion
35. Salt Bath Descaling
36. Solvent Degreasing
37. Paint Stripping
38. Painting
39. Electrostatic Painting
40. Electropainting
41. Vacuum Metallizing
42. Assembly
43. Calibration
44. Testing
45. Mechanical Plating

These processes generally cover all the process water discharge at metal finishing plants. The problem of plants having to separate wastewaters to comply with a variety of regulations applicable to different processes has been essentially eliminated.

III. POTW Removal

Continuing complaints have been raised that while POTW's remove pollutants and industry pays for this treatment, EPA's regulations do not account for it. The Agency did develop a procedure for POTW's to obtain

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*Publically Owned Treatment Works.

removal credits. The removal credit section of both the June 26, 1978 and January 28, 1981 general pretreatment regulations has been criticized as being so burdensome and unworkable as to discourage sewage treatment works from granting them.

Removal credits are a direct outgrowth of statutory requirements. The statutory authority for removal credits is found in a 1977 amendment to section 307 (b) (i) of the Clean Water Act. The availability of removal credits is subject to a number of conditions. First, and most obviously, there must be some demonstrable removal of toxic pollutants by the POTW. A second requirement is that the discharge from the POTW " . . . not violate that effluent limitation or standard which would be applicable to [the toxic pollutant removed by the POTW] if it were discharged by [the industrial source] other than through a [POTW]." A third requirement is that the removal of toxic pollutants by the POTW not cause the POTW to violate sludge use or disposal requirements under section 405 of the Act. A fourth requirement is that the POTW develop a local compliance program.

The revised credits package, recommended for proposal with the Metal Finishing category, does not deviate from this basic plan. The new removal credits package simplifies and renders more flexible compliance with the statutory requirements. Easily the most important change is the provision for "national removal rates." The proposal provides that POTWs which have complied with secondary treatment requirements, or are close to meeting those requirements, may demonstrate consistent removal by reliance on "national" removal rates developed by EPA, rather than through collecting data on their individual removal performances. Other important changes are the elimination of the combined sewer overflow requirements and the simplification of approval procedures. The staff recommendations are listed below.

Pollutant	*Removal Credit*
Cadmium	38%
Chromium	65%
Copper	58%
Nickel	19%
Zinc	65%

(Caution: These values are based on the 25th percentile. Industry may desire the 50th percentile values which would result in slightly greater removal credits.)

As an example of the effect of these removal credits one can examine Electroplating Pretreatment.

Current Pollutants	*Limits Daily Max. (mg/l)*
Cadmium	1.2
Chromium	7.0
Copper	4.5
Nickel	4.1
Lead	0.6
Zinc	4.2

After application of removal credits:

Pollutant	*Daily Max. (mg/l)*
Cadmium	1.9
Chromium	20.0
Copper	12.7
Nickel	5.1
Lead	1.2
Zinc	12.0

IV. Separation and Economic Impact

The Agency estimated significant potential closures among job shops and independent printed circuit board manufacturers, 19.9 percent for job shops (3.1 percent of all printed circuit board manufacturers, however, closures are concentrated among independents). In accordance with the Settlement Agreement with NAMF the Agency is separating existing source pretreatment standards for job shops and independent printed circuit board manufacturers from the Metal Finishing regulations. This division essentially amounts to a separate subcategorization of the economically vulnerable segment of the industry. The current less stringent Electroplating Pretreatment requirements will remain in effect for both job shops and independent printed circuit board manufacturers. With the installation of removal credits, further reduction in impacts is anticipated. An examination of effluent data from job shops indicates that approximately 15 percent of the facilities without precipitation/clarification will not require additional treatment due to removal credits. This amounts to a capital cost savings of approximately $28 million for job shops. Even more substantial savings may occur due to plants installing less expensive technology to meet the relaxed values.

Finally, the following illustrates the Metal Finishing regulation, which is based on precipitation, clarification, cyanide destruction, hexavalent chromium reduction and toxic organic disposal.

	Concentration (mg/l)	
Parameter	*Daily Maximum*	*30-Day Average*
TSS	61.0	22.9
Cadmium	1.29	0.27
Chromium, Total	2.87	0.80
Copper	3.88	1.09
Lead	0.44	0.15
Nickel	3.51	1.26
Zinc	2.57	0.81
Silver	0.44	0.13
Oil and Grease	42.4	16.7
Total Toxic Organics	0.58	—
Cyanide, Total	1.30	0.28

After implementation of removal credits these daily limitations are higher than the previous Electroplating Standards without removal credits.

Pollutants	*Daily Max. (mg/l)*	*30 Day Max. (mg/l)*
Cadmium	2.08	0.44
Chromium	8.20	2.29
Copper	9.24	3.88
Nickel	4.33	1.56
Lead	0.85	0.29
Zinc	7.34	2.31

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

Status of EPA's Hazardous Waste Program

Gary N. Dietrich*

It is my purpose in this presentation to provide you with a current status of the hazardous wastes regulations under The Resource Conservation and Recovery Act (PL 94-580) and a projection of where this program is going, particularly as it relates to the electroplating industry. The Phase I regulations were promulgated in May 1980 and became effective in November 1980. These regulations contain standards applicable to hazardous waste generators, transporters, and owners and operators of hazardous waste treatment, storage, and disposal facilities. Several electroplating wastes and metal heat treating wastes are listed in the regulations. The characteristics applicable to some unlisted electroplating wastes may render them hazardous as well. Two principal changes have been made since the May 1980 promulgation. First, the Extraction Procedure characteristic was modified, with respect to chromium, so that it is now based on hexavalent chrome rather than total chrome. The interim final amendment, including the test procedure for hexavalent chrome, will soon be finalized. Secondly, we have delisted several listed wastes which contained trivalent rather than hexavalent chrome as their principal chromium species.

Let me give you a status report on delisting. The delisting process is working well. It's certainly working a lot better than I had suspected it would when first created back in May 1980. We have received 118 delisting petitions with regard to electroplating wastes to date. We have granted temporary delisting for 73 of those. We have denied four. Three have been sent to their respective States which have the interim status program, and therefore are responsible for delisting. Eight have just been received, while 30 are presently under review. Overall, this equates to a 97 percent average in granting delisting petitions for electroplating wastes.

A subject closely related to the listing and delisting of wastes is the definition of a solid waste. There has been a great deal of confusion in the regulated community with regard to the definition that appeared in the May 1980 regulations as it relates to wastes that are used, reused, recycled, or reclaimed. We have been working very hard over the last year and a half with regard to modifying that definition and have worked extensively with petitioners in litigation who have raised questions about that definition. We have gone through no less than 33 drafts of a redefinition. We think we're about at the point where we'll have something that will better define what we intend to call a solid waste with regard to the jurisdiction of this program. And without going into a great deal of detail let me give you a sense of the basic issue we're dealing with. When a waste is used, reused, recycled, or reclaimed, the jurisdiction of the hazardous waste program over those wastes must be established. If wastes are burned as a fuel we would ultimately want to bring that under our jurisdiction. If wastes are used in a manner that constitutes disposal like a soil conditioner, fertilizer, or a deicer, we would want to have jurisdiction over them. On the other hand, we do not want jurisdiction over wastes that are recycled or reclaimed on site as an integral part of a manufacturing operation. To the extent that wastes are sent off site for reclamation, we do, in a selective way, want to regulate some of those operations. That gives you a general sense of what changes you might see in the redefinition of solid waste. We hope to propose this redefinition in the latter part of March.

In the generator and transporter standards area, the principal change that is underway is the development of a uniform manifest which would apply to interstate and intrastate shipments. We are working on this cooperatively with the Department of Transportation (DOT). This uniform manifest would be preemptive, in that the States would be preempted from using any other manifest under DOT regulations. After the current OMB review is completed and clearance is obtained, the package will go into the Federal Register as a proposed change. Of course, we would take public comment, and ultimately promulgate a uniform manifest unless we received adverse comments. We generally have worked on that issue with the States and with an industrial interest group, principally representing transportation interests, and believe we have reached a general concurrence among the regulated community and the States as to what constitutes an adequate uniform manifest. So we have tried to do our homework and grease the skids for a fairly successful rulemaking.

A number of changes have been made, or are in progress, in the interim status standards area. You may recall that, in the fall of 1980, we dealt with the issue of whether interim status standards would apply to wastewater treatment processes which are handling hazardous wastes. At that time, we proposed substituting, for interim status standards, what amounted to a permit-by-rule which would establish about a dozen major requirements for those types of facilities. To enable time to complete that proposed rulemaking without imposing the interim status standards on those types of facilities, we suspended interim status standards with regard to wastewater treatment processes conducted in tanks or containers where they are connected to an industrial process. That suspension is still in effect. We still have yet to complete the proposed rulemaking process. We have analyzed all of the comments and I would say in another month or two we would be coming out with final

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promulgation on the permit-by-rule for those types of facilities. For now, however, that issue is on the back burner because we are working night and day on land disposal standards which I'll talk about later.

Several questions have been recently raised concerning the status of regulations pertinent to liquids and landfills. You may recall that the May 1980 regulations placed a deferred requirement that liquids in bulk form and in containers could not be disposed in landfills after November 1981. The rule was conditional in that bulk liquids could be disposed of in a landfill if there was a liner and a leachate collection system. However, with regard to containers, there was an absolute ban. Containers containing any amount of free liquid, even one drop, could not go into a landfill after the November 1981 date. A number of people have questioned that rule and it also was brought up in litigation. We negotiated with the litigants in the September/October period and came to a settlement in the very early part of November. We developed a proposed rule pursuant to that settlement. Basically, this rule does relax the requirement on containerized liquids being placed in landfills.

It provides a formula which allocates a percentage volume ranging from 0 to 25 percent of the landfill to be devoted to the placement of containerized wastes having any amount of free liquid in them. On the average, the formula should allow about 10 percent volumetric free liquids in containerized wastes to be placed in landfills. That's the objective we were trying to seek. In the mean time, the ban on liquids is in effect and we will exercise enforcement discretion with regard to violations in this interim period, recognizing that we do have a prosposed rule and a suspension in the process.

There was some talk that the groundwater monitoring requirements which were also to take effect on November 19, 1981, would not take effect. They indeed did take effect and groundwater monitoring systems were supposed to be installed and in operation at land disposal facilities by that date. We are soon going to be promulgating an interim rule which would revoke the previous rule requiring submission of an annual report. Our strategy will be to collect information for an annual survey which will review about 10 percent, instead of 100 percent, of the regulated community each year. This is not to say that people are relieved of recordkeeping and recordkeeping requirements, particularly operating plans. It is to say, however, that only those people who are part of the 10 percent survey must submit an annual report.

Another important change in the regulations concerns financial responsibility. You may recall that our regulations require proper closure of a facility, and for land disposal facilities the regulations require post-closure monitoring and maintenance. To assure that the monies are available for these operations, we promulgated, in January of 1981, financial assurance requirements that require facility owners or operators to put money aside in a trust fund or other instruments, such as performance bonds or surety bonds. Since then we have been working on two other instruments that would enable people to put money aside. One is a financial test to self-assure that monies would be available. This device would be principally helpful to larger corporations with assets of more than 10 million dollars. Another device would be an insurance policy which could be purchased to insure that money is available to cover those types of costs. If OMB clears the amendment providing these two additional instrumets, we will publish this amendment to the January regulations. The effective date of the January regulations has been suspended to April of this year, in the hope these additional instruments can be added before that effective date. You probably also have read that this Administration is about to propose a suspension of the liability insurance requirements which were also promulgated on January 12, 1981, and which were to take effect in July of last year. We have received OMB clearance with regard to a proposed rule to that effect. The rule, which will be out in about another 30 days, will propose elimination of liability insurance for treatment, storage, and disposal facilities. We will take public comment on this rule and, based on those comments, determine whether to go through with that suspension. I think those are the major changes affecting the Phase I regulations.

Phase II regulations set the standards which are to be used in permitting treatment, storage, and disposal facilities. In January, 1981, we promulgated the Phase II standards governing storage, treatment and incineration. We also promulgated on February 13 a temporary standard governing the permitting of new land disposal facilities and on February 5 reproposed regulations dealing with the permitting of existing land disposal facilities. The regulations dealing with storage, treatment, incineration, and new land disposal facilities did indeed go into effect in July and August. The Agency will be using these regulations to call in Part B applications with regard to existing facilities and to write permits for those types of facilities. The standards for existing land disposal facilities are still in a proposed stage, but we were recently ordered by the District Court of the District of Columbia to promulgate those standards by February 1 of this year. We think that we have a reasonable and workable standard that can be promulgated for existing land disposal facilities. I do not think that we can physically make the February 1 deadline, but believe we can complete this task sometime between March 1 and April 1. We indeed are going back to the Court to ask for a reconsideration. As I say, I think we have a standard that will be workable. I can't give you all the details of that standard because I would be violating ex parte. I can, however, give you an indication that the standard is likely to be an environmental performance standard. It will not require that arbitrary retrofitting of existing land disposal facilities as would technology-based standards, which was one of the principal criticisms we received from the regulated community with regard to a previous proposal on land disposal facilities.

Given that we have the regulatory program in place, how does regulatory reform affect the hazardous waste program? There are two things in regulatory reform that we are responsible for dealing with. One is the Executive Order 12291 which essentially requires that those regulations that were not effective the date this Executive Order was issued should not go into effect until a complete regulatory impact analysis had been done. Principally, that affected the Phase II regulations, promulgated in January and February concerning the permitting of storage, treatment, incinerators, and new land disposal facilities. However, this Executive Order indicated that we could allow the Phase II regulations to go into effect without a regulatory impact analysis if there was good cause to do so. We indeed did do that. The cause was that we were under a court order in the first place to promulgate those regulations.

OMB approved this action, but with the condition that we would perform a regulatory impact analysis on those standards during calendar year 1982, and that we would subsequently proceed with any amendments that are indicated by that analysis and ultimately finalize the standards during calendar year 1983. So to simplify it, the storage, treatment, and incinerator standards which are in effect today will go through a regulatory impacts analysis during this calendar year. Some amendments will probably be added before the standards are finalized toward the end of 1983. The situation is basically going to be the same for land disposal standards. In promulgating those standards to meet the February 1 court order, we will establish a standard without going through the regulatory impact analysis. We will do the regulatory impact analysis after the fact and produce the changes deemed necessary by that analysis before the end of 1983. In essence, we hope to have, if you will, all of our standards in final form by the end of 1983. In the interim, these standards will be used for both permitting and authorizing states.

Now I would like to direct my discussion toward the possible results of the places in our regulations where we can tailor the regulatory requirements to deal more carefully with the degree of hazard by lessening requirements for those wastes which are less hazardous than others and increasing requirements for those wastes that produce a particular high degree of hazard. A tailoring of the technical requirements of our regulations, both in the storage and treatment areas, as well as in the land disposal area will occur. With regard to land disposal, some wastes are hazardous because they fail the EP toxicity characteristic. However, in some cases, these wastes are not codisposed with organic wastes; in addition, they may pass a neutral-water EP toxicity test. In these situations, we think some lesser requirements can be applied. Some examples of such wastes are foundry wastes. We believe a great many foundry wastes could pass a neutral-water EP test and are not co-disposed with municipal wastes, but instead are "monofilled." We believe we can give a lesser set of requirements to these types of wastes. A liner or leachate collection system will probably not be required. The cover requirements at closure could probably be lessened. Another example of tailoring the technical requirements of our regulations concerns facilities that neutralize wastes which are hazardous solely because of their corrosivity. Again if that neutralization takes place relatively soon, we believe requirements for lining and groundwater monitoring may not be necessary. Finally, with respect to storage facilities, if a waste is hazardous only because of its metal content, and is a non-liquid waste, we're not quite sure that you need secondary containment, some of the inspection programs, or some of the contingency plans that would otherwise be required of other types of hazardous wastes. So that gives you two examples of some of the tailoring we are considering.

On the other end of the scale, however, we may develop more stringent requirements for land disposal of certain wastes. We might ban the disposal of certain highly toxic or persistent solvents from land disposal.

Another area that we're looking at is the class permit. Those who follow the water program may be familiar with the general permit used in the 404 dredge and fill program. This would be a similar type of permit. Instead of trying to permit individual facilities, we would try in some cases to permit a number of facilities which have some commonality. In doing this we would reduce a lot of the permitting paperwork, both on your part and on the permittee's part, and therefore save time and frustration for all concerned. We are working very hard to develop a set of class permit procedures that would go into the consolidated permit regulations. We are hopeful that we can get those procedures developed and proposed in late February or early March. In some sense, coming up with a class permit procedure may be the most meaningful thing we are doing in the regulatory reform area.

While we're doing all of the foregoing activities, we will continue the fine-tuning of our regulations as we see major problems crop up that should be dealt with to make the program workable. For instance, we are soon going to come out with a set of amendments to take care of some of the problems concerning our incinerator standards so the program can work effectively.

Three other areas that I should address are statutory changes, state authorization, and consolidated permit regulations. The Resource Conservation and Recovery Act comes up for reauthorization this year. Reauthorization of appropriation authority usually provides an opportunity to make changes to the statute. At this point, the Agency does not intend to ask for substantive changes to the statute this year. The predominant thinking is to try to make this program work with our current statutory authority, to get the regulations out and have them become effective, and to go through the regulatory impact analyses before we tinker with the statute. At the end of that time, if real reason for statutory change exists, we will then go in for changes. I have a suspicion that Congress is not particularly interested in dealing with statutory changes in the RCRA during this year either since they have other major problems to deal with such as the Clean Air Act and the Clean Water Act.

Most people are aware that the statute enables us and, indeed, encourages us to authorize the program to the States. We are doing that and it is a high priority for the Agency, for this Administration. Currently, we have 27 States that have been authorized for Phase I of the program. We hope that the number will move up to the 35 to 40 area before the end of this year. No States have yet been authorized for Phase II, however, most of the States that now have Phase I are expected to come in for Phase II. We think the Phase II authorizations will lag those of Phase I by about 1 year. I mentioned earlier that in meeting the February 1 court order, we would have put our last regulation in place. Therefore we would be in a position to begin the timeclock for full authorization of the States rather than interim authorization of the States. That decision has not been made, but it is a decision that is likely to be considered within the next 30 to 45 days. The inclination of the Agency at this time as far as I know, with all regulations in place, is to allow the States to have the option of going directly into full authorization by the fall of this year.

Lastly, there are several changes developing in the area of the Consolidated Permit Regulations, which cover RCRA and other permits. These changes are the result of the settlement of litigation. Negotiations took place in the spring and summer of last year and culminated in a settlement around September. There are some 24 changes in that settlement that affect the RCRA permit regulations which are part of the consolidated permit regulations. I will address the three most important ones. The first involves a change in the requirements for modification of interim status. Basically, what we're saying there is that we would allow interim status land disposal and incinerator facilities to expand up to 50 percent, and storage and treatment facilities could expand an unlimited amount, without having to first obtain a new permit. Another is to change from a 10 year RCRA permit to a lifetime RCRA permit. In doing this, however, we have asked for more reopener clauses, particularly the ability to reopen a permit if there is a significant change in our regulations. And finally there was an amendment that would deal with the so-called construction ban. Currently, new facilities cannot begin construction until they have a RCRA permit. The change would relax that with regard to storage, treatment and incinerator facilities and allow construction to begin without a permit but, indeed, require a permit before operation begins. However, with regard to land disposal facilities, a permit would be required before construction begins. These are the three most important items resulting from the NRDC settlement concerning the consolidated permit regulations. Those changes will need to be proposed and go through the proposed rulemaking before they are promulgated. We would expect that those proposed rules would be published in the Federal Register within the next couple of months. I think that covers the essential items of the status and direction of the hazardous waste regulatory program at this time.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

RCRA Delisting Procedures And a Regulatory Overview

Alfred B. Craig, Jr.*

INTRODUCTION[1]

EPA has promulgated regulations designed to manage and control the country's hazardous wastes from generation to final disposal. These regulations are a result of a directive to EPA by Congress in the Resource Conservation and Recovery Act (RCRA) of 1976 (Public Law 94-580). Congressional concern was prompted by the large quantities of solid wastes being generated.

The RCRA regulations are to control activities of generators, transporters, treaters, storers and disposers of hazardous wastes. They differ from those regulations concerned with air and water pollution in that air and water regulations vary according to the specific industry (for example, electroplating) to which they are directed. In contrast, all industries that generate, store, haul, or dispose of hazardous wastes must comply with the same sets of rules. Most owner/operators of electroplating facilities will be considered generators of hazardous wastes and may be considered to own or operate treatment, storage, or disposal facilities. The procedures to determine if wastes are hazardous and the requirements for generators, storers, and disposers of hazardous wastes follow.

Identification of Hazardous Wastes

Under the Hazardous Waste and Consolidated Permit Regulations promulgated on May 19, 1980, solid wastes include all substances destined for disposal and not already regulated by the Clean Water Act or the Atomic Energy Act of 1954.

EPA has developed the following methods of listing wastes as criteria for determining which solid wastes must be classified as hazardous. A waste may be listed in the Federal Register, it may be tested and determined hazardous, or the generator can admit that it is hazardous.

Tests for: Ignitability
Corrosivity
Reactivity
Toxicity of leachates

are used to list or delist wastes. A waste possesing one or more of these traits will be declared hazardous.

The following electroplating wastes are listed as hazardous unless proven otherwise:

Wastewater treatment sludges (toxic)
Spent plating bath solutions (reactive, toxic, & corrosive)
Sludges from the bottom of plating baths (reactive, toxic, & corrosive)
Spent stripping and cleaning bath solutions (reactive, toxic, & corrosive)

The corrosivity criterion is used to determine if these materials can extract toxic contaminants from other wastes or make them soluble. A material is corrosive if it has a pH below 2 or above 12.5, or if it corrodes steel (following a test developed by the National Association of Corrosion Engineers).

Reactive wastes have one or more of the following tendencies:

To autopolymerize
To create a vigorous reaction with air or water
To exhibit thermal instability with regard to shock or to the generation of toxic gases
To explode

The final characteristic, toxicity, is one of most importance to electroplaters. If disposed of improperly, toxic wastes may release toxic materials in sufficient amounts to pose a substantial hazard to human health or to the environment. EPA has designed a leaching test (called the Extraction Procedure) to measure the amount of toxic materials that can be extracted from the waste at a pH of 5, during a 24-hour period, with constant stirring. If the extract obtained from the test exceeds set limits for certain contaminants, the waste will be considered hazardous. Eight metals are among the 14 materials selected as toxic;

Table I
Toxic Waste Limits Set by EPA's Extraction Procedure

Pollutant	*Extract level (mg/L)*
Arsenic	5.0
Barium	100.0
Cadmium	1.0
Chromium	5.0
Lead	5.0
Mercury	0.2
Selenium	1.0
Silver	5.0

SOURCE: U.S. Environmental Protection Agency. "Hazardous Waste Management System: Identification and Listing of Hazardous Waste." Pt. 3. *Federal Register*. 45(98):33084-33133, May 19, 1980.

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several of these metals are commonly used in electroplating. Table I lists the specific metals with the standard for each. Other materials may be added to the list in the future.

Requirements for Hazardous Waste Generators

Producers of hazardous waste are considered generators under the regulations. It is a generator's responsiblity to determine if the waste is hazardous by 1) consulting the lists, 2) conducting EPA-specified tests, or 3) the generator may simply declare the waste hazardous. If the waste is known to be nonhazardous, testing is not necessary; however, the generator is responsible for the accuracy of that determination.

Generators of hazardous wastes are responsible for notifying EPA of their activities, using appropriate containers, labeling the containers, and ensuring proper disposal. The law also requires generators who produce and dispose of more than 1,000 kg (2200 lb) of hazardous waste per month, with certain exceptions, to use a manifest system to ensure proper transport and disposal.

The manifest records the movement of hazardous wastes from the generator's premises to an authorized off-site treatment, storage, or disposal facility. The manifest, signed by the generator, transporter, and disposer, is an official record that all Department of Transportation (DOT) and EPA requirements have been met. The generator must maintain original copies for 3 years, and must report to EPA if the manifest is not returned in 45 days documenting its arrival at its approved destination.

Exception reports are required, listing any unreturned manifests. Annual reports, documenting shipments of all hazardous wastes originating during the report year, also are required. In general, all information submitted by a generator is available to the public to the extent authorized by the Freedom of Information Act and EPA regulations associated with that act.

Requirements for Treatment, Storage and Disposal Facilities

When wastes are stored on site for 90 days or longer, the generator falls under an additional set of regulations designed to control owners and operators of hazardous waste storage and disposal facilities. The standards for storage promulgated in May 1980, are intended to prevent the release of hazardous wastes from storage areas into the environment. Hazardous wastes must be stored in tanks and containers that meet specifications established by EPA for the storage of flammable and combustible liquids. Beyond these specifications, materials compatible with the hazardous wastes must be used to construct or to line the containers.

Storage areas must have a continuous base impervious to the material being stored and must be designed for spill containment with either dikes or trenches, which require daily visual inspection. Throughout the storage period, records must be maintained showing the identity and location of all stored hazardous wastes. Site selection requirements apply, and leachate monitoring may be required. Obviously, it is an economic advantage not to be classified as a storage facility by default.

As stated earlier, these standards only apply to those who store hazardous wastes for 90 days or more.

Information Requirements for Temporary Exclusion of Electroplating Wastes

It is possible for a waste generator to petition to EPA for an exclusion of his waste from RCRA's hazardous waste requirements. If granted, then they are not considered hazardous. The applicant must submit the following information to the Administrator of EPA:

(1) Description of the manufacturing processes which produced the listed waste.

(2) Description of the waste treatment system (including chromium reduction, cyanide destruction, neutralization, flocculants added, etc).

(3) Schematic diagram of the waste treatment system.

(4) Average and maximum volume/tonnage of waste generated per month and per year.

(5) Disposal scenario used for waste generated prior to November 19, 1980, and the scenario proposed for the waste if an exclusion is granted.

(6) Total constituent analysis of the sludge (complete acid digestion) for each of the EP toxic metals and nickel.

(7) Analysis of the sludge for total cyanide. If the concentration recorded is greater than 1 ppm, test the sludge for free cyanide. If cyanide is used in the manufacturing process, a minimum of four samples should be tested. If cyanide is not used, the test result from one sample is sufficient.

(8) EP toxicity test results for cadmium, hexavalent chromium, and nickel. Test results should be submitted on samples obtained over a period of time to address any variability of constituent concentrations in the sludge (a minimum of four samples analyzed to this effect are required).

(9) EP toxicity test results for cyanide. Test results should be submitted using the EP extraction procedure but substituting distilled water for acetic acid.

(10) All EP toxicity tests should be performed using the method of standard additions. All recovery results should be reported.

(11) Explain any data point that deviates from the range identified by the other reported analyses.

(12) For each constituent not utilized in electroplating operations, the results from one total constituent analysis and one EP test should be submitted. In addition, a statement that these constituents are not used in the process is required.

(13) Information requirements as specified in 40 CFR 260.22(i) 1-12 (omit #7). This requirement applies to all inorganic wastes.

The generators petition must refute all of EPA's reasons for listing the waste. It is important to note that delisting of a generator's waste stream was not intended as a panacea for "compliance" with RCRA. Those plants with truly hazardous wastes will remain in the system. It was intended, however, to exclude those companies which, because of the procedural or definitional requirements of the regulations, had been inadvertently or incorrectly included in a regulated category. These companies may petition for an exclusion because their wastes truly are non-hazardous.

The EPA's hot line number is 800-424-9346 (202-382-3000 where RCRA questions can be answered.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

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[1] *Environmental Regulations and Technology: The Electroplating Industry*, EPA 625/10-80-001, August 1980.

Determination of the Relationship Between Plant Operating Conditions and Wastewater Sludge Leachability

Andrew Procko*

INTRODUCTION

A recent study[1] conducted cooperatively between the American Electroplaters' Society (AES) and the Industrial Environmental Research Laboratory, U.S. Environmental Protection Agency (EPA) evaluated the leaching characteristics of sludges generated by electroplating wastewater treatment systems. In this study 12 plants' sludges were characterized. One of the recommendations resulting from this work was to further investigate what effect the primary operating variables of the treatment system had on both the effluent quality and the leachability of heavy metals from the sludges. This paper presents the results of such an investigation.

Untreated wastewaters were collected at the plant and shipped to the laboratory where they were subjected to a number of treatment tests in which the treatment chemicals and pH were varied. Metal concentrations in the effluent and sludge extract were monitored.

The goal of this research was to characterize operations and sludges from six plants carrying on a wide variety of plating operations so that the information developed would be applicable on an industry-wide basis. The six plants were selected from the 12 that had participated in the EPA-AES study mentioned above.

DESCRIPTION OF PLANT, PLANT PROCESSES, AND SAMPLING

Plant Selection Criteria

Selection was based on the variety of metals utilized, the wastewater treatment system, and the leaching characteristics of the plants' sludges. The presence of cadmium in the plants' wastewaters was highly desirable as cadmium appears to be a problem metal with regard to its leaching characteristics. The plants designated as 2, 3, 4, 6, 7 and 8 were selected for this study, as previous testing had shown significant quantities of Cd, Cr, Ni, Zn, Cu, and Al present in wastewaters and sludge from these facilities. Other contributing factors included: good cooperation from plant management and the fact that the plant sludge had metal levels that EPA would consider hazardous based on results from the EPA Extraction Procedure (EP). The limits above which EPA considers EP results as hazardous are shown in Table 1.

Cyanides were oxidized at three plants with either sodium hypochlorite or chlorine in an alkaline environment. The treated chromium and/or cyanide waste streams were then combined with the other acid/alkali waste streams where pH adjustment with lime occurred in most plants. Generally, all six plants had their pH set-point at 10. Four plants added flocculating agents to the combined wastewaters to improve settling of the metal hydroxides in the clarifier. Overflow from the clarifier was discharged to the plant sewer while underflow went to further thickening and/or dewatering before disposal.

Two plants were using integrated treatment at the time of this study. The chemical treatment of the rinse water was integrated into the operation of the plating line. Integrated treatment involved continuously treating rinse waters during, or immediately after, the rinsing process. One plant had a treatment tank and feed sump corresponding to each rinse tank. The rinse water was continuously circulating from the rinse tank to the sump to the treatment tank and back to the rinse tank in a completely closed-loop fashion. Water was added only when required to adjust the tank level. The continuous treatment of the rinse water produced increasing quantities of metal hydroxides that were recirculated back to the rinse tank. The metal hydroxides were settled out daily and transferred to another settling tank, and finally filtered. Another plant used integrated treatment for its CdCN rinse water. The cyanide rinse tanks were used as the first stage of cyanide oxidation. A slip-stream of this treated rinse water was combined with all other cyanide rinse waters and sent through a second stage of cyanide oxidation, and then further treatment.

Sample Collection

During the preliminary study mentioned earlier, detailed

Table 1
Maximum Concentration of Metals for Characteristic EP Toxicity

Metal	*Maximum Concentration (mg/l)*
As	5.0
Ba	100.0
Cd	1.0
Cr	5.0
Pb	5.0
Hg	0.2
Se	1.0
Ag	5.0

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[1] *Meredith, J. W., McCarthy, J. A. and Procko, A., Electroplating Wastewater Sludge Characterization. EPA-600/S2-81-064, U.S. Environmental Protection Agency, Cincinnati, Ohio, 1981.*

plant data were not collected. Therefore, a 1-man presampling survey was required to identify the plating operations; type and quantity of rinses, potential sampling sites; number of samples required; and the operating procedures and chemicals for the wastewater treatment system. After completion of a sampling plan for each of the plants, a sampling team of one or two men, depending on the size and complexity of the plant, visited each plant, noted the flow rates of individual streams where necessary, and observed operations for anything unusual.

Liter samples were taken in order to allow for an evaluation of the performance of individual subsystems, such as chrome reduction, and the overall Wastewater Treatment System (WWTS). As it was impossible to collect an untreated sample of a plant's combined wastewater, the individual wastewater samples were combined in the laboratory in proportion to their relative flow rates in the plant. Fifty-five gallon drum samples to be used in the experimental program were taken of all wastewater streams at locations upstream of the plant's pH adjustment system.

For the six plants studied, the underflow from the plants' clarifier was sampled, as this would represent the feed to a mechanical dewatering system if one were present. For this study, it was decided that samples of underflow directly from the clarifier would more closely resemble the more general case of metal finishing treatment sludge than would sludge from a thickener or from a dewatering device. The underflow characteristics would then be used as a basis of comparison for the results of the testing program.

Retention times and flowrates for each treatment step were calculated from data obtained in the plant. If capacities of waste treatment tanks were not readily available, tank measurements were made by the survey team. Flowrates were confirmed by several methods. These include: counting rinse tanks and measuring overflow rates, including some allowance for cooling water, condensate, sanitary water, etc.; reading water meters when available; and measuring the inflow and outflow of wastewater sumps. From flowrates and tank capacities the retention times were calculated. Table 2 contains the analytical test results for actual plant samples.

Plant Operations

Plant 2 is a captive shop which uses chromate dips and plates acid Zn and acid Cd onto metal screws. One barrel line is present in the plant and serves both plating tanks.

Plant 3 is a job shop which barrel and rack plates cadmium and copper, as well as using solder and chromate dips.

Plant 4 is a job shop which plates Cu, Ni, and Cr onto zinc die-castings. One manual rack line is present in the plant.

Plant 6 is a captive shop which plates nickel and chrome onto steel. One automatic rack line is used for plating, and one manual rack line is used for stripping.

Plant 7 is a job shop which plates brass, bronze, cadmium, chromium, copper, nickel, and zinc. The plant also anodizes and bright dips aluminum.

Plant 8 is a job shop which plates copper, nickel, and chrome onto plastic. The system is composed of one manual rack plating line. Plating onto plastic requires that

Table 2
Analytical Test Results for Actual Plant Samples (mg/l)
Plant 2

Sample Description	*pH*	*TDS*	*TS*	*Cd*	*Cr*^{1}	*Cr*$^{+6}$	*Zn*
Yellow Chromate	1.59	28.000	35.100	25.4	19.070	770	3.020
Zinc Bath	5.43	168.200	270.000	0.37	<0.1		22.500
Cadmium Bath	1.98	87.500	99.500	14.600	8.49		1.850
Acid Bath	0.74	7.760	12.500	372	1.57		645
Effluent	11.15	16.100	16.100	3.68	6.08	0.08	7.73
				0.37*	0.20*		0.66*
Spent Acid	1.72	2.530	4.920	38.6	66.8	<0.05	499
Blue Chromate	0.62	27.300	31.300	0.94	343	74	2.580

Plant 3

Sample Description	*pH*	*TDS*	*TS*	*Cd*	*Cr*^{1}	*Cr*$^{+6}$	*Zn*	*CN*	*Cu*
Clear Chromate	7.18			3,980	2.02	<0.05			
Yellow Chromate	12.38			0.91	705	685			
CdCN Rinse	12.76			—				298.7	
Other CN Rinse	10.81			60.5				42.2	2.70
Acid Rinse	11.97			54.5					11.4
After CN Oxidation	11.22			—				31	
After pH Adjustment	10.90	4.430	5.640	69.5	45.8				2.18
Effluent	11.75			2.90	14.9		0.82		
				1.68*	10.5*		0.51*		1.58*
Centrate	10.43			10.4*	14.6*		4.42*		
Clarifier Underflow	10.36	5.940	10.700	538	3.55	1.52			
Acid Sump (Barrel)	10.86				1.46				5.17
Acid Sump (Rack)	4.32			106	252				0.76
After CN Oxidation	10.76			2.46					0.09

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*Dissolved Metal.

Table 2

Plant 4

Sample Description	pH	TS	TDS	Cr^{1}	Cu	Ni	Zn	CN(diss)
Treated Cyanide	10.07							5.75
After pH Adjustment	12.07			1.33	42.3	31.1		
Effluent	11.70			1.51	1.15	2.65		
				0.92*	0.11*	0.96*		
Filtrate	11.88			1.30*	1.41*	2.43*		
Treated Cyanide	10.01			0.62	80.6	15.8	0.36	
Ni Rinse	7.32			2.09	6.57	165	2.59	
Cleaner Rinse	9.13			0.34	0.75	0.33	25.0	<0.02
Sludge	10.66	138,000	8,200	158	34.9	55.3	25.0	<0.02

Plant 6

Sample Description	pH	TS	TDS	Cr^{1}	Cr^{+6}	Ni
After Mix Tank	11.56	5,250	2,000	<0.5*	<0.05	<0.1
Clarifier Overflow	11.80			<0.5*	<0.05	<0.1
Effluent	9.79			<0.5	<0.05	<0.1
				<0.5*	<0.05*	<0.1*
After CR Reduction	1.93			352	<0.05	2.59
Combined Acid Rinse	2.63			45.6	<0.05	18.5
After Mix Tank	12.36			1.11	<0.05	0.35
Sludge from Clarifier	11.78	81,100	1,940	45.6	<0.05	18.5

Plant 7

Sample Description	pH	TS	TDS	Cd	Cr^{1}	Cr^{+6}	Cu	Mn	Ni	Zn	Al	CN_1
Acid/Alkali	6.71	1,080		0.10	0.67	<0.05	1.35	0.30	43.0	13.0	0.62	
Acid/Alkali	6.88	994		0.06	0.49	<0.05	1.31	0.26	55.5	12.5	0.58	
Untreated Cr	2.23	810		<0.01	50.0	6.60	0.12			180.0		
Treated Cr	1.55	1,850		<0.01	44.5	<0.5	0.11	0.14	<0.10	143	0.75	
Untreated CN	7.69	7,510		25.2	<0.1		10.2	0.10		265		21.5
Untreated CN	12.13	3,040		20.2	0.05	<0.05	8.12	0.18	<0.10	137	0.50	440
Treated CN	3.26	7,880		13.5	0.08		6.0	0.15		215		4.40
Untreated Al	2.41	1,520		0.04	0.52	<0.05	0.80	0.25	0.98	4.48	78.0	
Combined Streams	8.5	2,360	1918	0.08	3.05		0.85	0.13	10.0	27.3	20.6	
Clarifier Effluent	10.1	2,280	2226	<0.01	0.25		0.10	<0.05	3.6	2.88	9.9	
Clarifier** Underflow	8.53	7,850	2150	0.14	4.72	<0.05	2.98	0.90	165	762	0.75	
Underflow Sludge Bed**				4.75	0.50	<0.05	1.32	2.62	46	516	1.12	

Plant 8

Sample Description	pH	TS	TDS	Cr^{1}	Cr^{+6}	Cu	Ni
After pH Adjust	9.64	4,100	2,500	298		43.5	37.7
Clarifier Overflow to Effluent	9.16			0.22		1.09	0.38
				0.10*		1.15*	0.55*
Filter Filtrate to Effluent	9.45			0.77		0.50	0.73
Chromium Waste	2.14	1,790	1,600	2,500	<0.05	48.5	55.0
Acid/Alkali Rinses	3.22	1,100	980	3.68		50.4	43.0
Clarifier Sludge**	9.84	11,900	2,400	111	0.08	16.1	44.1

*Dissolved metal.

**Metal concentrations are those found in the EP extract.

Plant 8 use an acid copper bath rather than alkaline copper cyanide.

Wastewater Treatment System Description

The wastewater treatment systems in use at each of the plants were typical of systems that segregate their waste streams for separate treatment. Five of the six plants reduced Cr^{+6} to Cr^{+3}—some plants more successfully than others. These five plants used reducing agents such as sodium bisulfite, ferrous sulfate, or sulfur dioxide in an acidic environment to carry out the chemical reduction.

TEST PLAN AND RESULTS

TEST PLANNING AND PREPARATION

The purpose of the overall test program was to determine the effect of wastewater treatment chemicals and pH on the leaching characteristics of the sludges generated. To accomplish these goals, a detailed test plan was prepared which covered: (1) wastewater preparation; (2) simulation of the plant treatment; (3) screening tests; and (4) analysis of the results. Screening tests were performed to determine the precipitation chemical and pH combination which produced a sludge with the best leaching characteristics without reducing effluent quality.

Plant simulation and treatment studies were also performed using 55-gallon drum samples of the individual waste streams collected at each plant.

SIMULATION STUDY

Samples of the individual waste streams in each plant were taken. These samples were combined in ratios proportional to their flow rates in the plant to simulate the plant's untreated wastewater. This simulated wastewater was treated under conditions as close to plant conditions as possible. The plant's chemicals were used for pH adjustment and flocculation, and residence times in the pH adjustment tank and clarifier were duplicated in these simulations.

Following settling, the supernatant was decanted. This sample, the simulated overflow, was analyzed for metals of interest and compared to the plant's effluent sample.

The simulated overflow was collected, extracted by the ASTM-A extraction procedure, analyzed for metals and compared to the ASTM-A extract of the plant's clarifier underflow. Good agreement between simulation experiments and actual plant samples suggests that results of subsequent laboratory treatment studies will be meaningful in the plant operating environment. Data are recorded in Table 3.

FLOCCULATION STUDY

Additional studies were conducted on portions of the simulated waste stream of each plant to determine an optimum polymer flocculating agent and its effective concentration. In this study, four anionic polymer flocculating agents were evaluated against the flocculating agent employed at the plant to determine which produced the best settling rates and flocculant characteristics. Since this was not intended to be a major area of this investigation the flocculating agent chosen and its optimum concentration were used throughout the remainder of the study. The results of this study were qualitative and are shown in Table 4.

Settling tests were performed by evaluating each flocculating agent over a concentration range of 0 (blank) to 8 mg/l.

Plant 2 used no polymer flocculating agent. Magnifloc 836A and Calgon WT-3000 performed well on its simulated waste stream. Magnifloc 836A was effective at a much lower concentration and was chosen for future studies.

Plant 3 also used no polymer to aid settling in their treatment. Very slow settling rate was observed without added flocculating agents. Only Calgon WT-3000 resulted in improved settling and floc characteristics. It was effective at a final concentration of 0.5 mg/l.

Plant 4 settled well using Separade P-3 (its own choice of polymer), Separan AP-273 and Calgon WT-3000. Separan AP-273 was chosen since it was effective at the lowest concentration.

Plant 6 used 6 mg/l Percol in its treatment. Percol was found to be effective at 2 mg/l. This was the only plant in which its flocculating agent outperformed the others investigated.

Plant 8 used EPEC Floc 306 which performed well at 5 mg/l; however, Separan AP-273 and Calgon WT-3000 were equally effective at lower concentrations. Separan AP-

Table 3
Results of Plant Simulation Tests
Plant 3

	pH	*TS*	*DS*	*Cd*	Cr^T	Cr^{+6}	*Cu*	*Ni*	*Zn*
Plant Underflow (ASTM-A)	10.36	10,700	5,940	0.04	0.95	1.39	0.17	<0.1	
Plant Simulation Underflow (ASTM-A)	10.9	11,000	4,450	0.33	0.11	0.80	1.00	<0.1	
Plant Simulation Underflow with Correction for Dilution				0.55	0.18	1.34	1.67	*	
Plant Effluent***	11.75			1.68	10.5		1.58	<0.2	0.51
Plant Simulated Effluent***	10.9			0.03	17.9		4.73	<0.1	0.05

Plant 4

	pH	*TS*	*DS*	*CN*	Cr^T	Cr^{+6}	*Cu*	*Ni*	*Zn*
Plant Underflow (ASTM-A)	10.66	138,000	8,200	<0.02	0.41	0.49	0.06	0.38	<0.1
Plant Simulation Underflow (ASTM-A)	10.5	58,100	—	—	<0.1	<0.05	2.05	1.96	0.02

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*Correction Factor Cannot be Applied.

***Analysis was for dissolved metal rather than total metal to determine the effectiveness of treatment.

	pH	Cr^{T}	Cr^{+6}	*Cu*	*Ni*	*Zn*
Plant Simulation Underflow with Correction for Dilution		*	*	6.86	6.56	0.07
Plant Effluent***	11.7	0.92	1.10	0.11	0.96	
Plant Simulated Effluent***	10.5	0.23	0.09	0.8[illegible]	10.0	

Plant 6

	pH	*TS*	*DS*	Cr^{T}	Cr^{+6}	*Ni*
Plant Underflow (ASTM-A)	11.78	81,100	1,940	1.12	<0.05	<0.10
Plant Simulation Underflow (ASTM-A)	11.70	29,800	3,840	0.19	<0.05	<0.25
Plant Simulation Underflow with Correction for Dilution				0.39	*	*
Plant Effluent***	11.80			<0.50	<0.05	<0.10
Plant Simulated Effluent***	11.70			<0.10	<0.05	<0.25

Plant 7

	Cd	Cr^{T}	*Cu*	*Ni*	*Zn*	*TS*	*DS*
Plant Underflow (ASTM-A)	.02	<.05	.04	.38	.65	7,774	2,074
Plant Simulation Underflow (ASTM-A)	<.02	<.10	.06	1.42	0.14	4,375	2,080**
Plant Simulation Underflow with Correction for Dilution	*	*	0.16	3.77	0.37		
Plant Effluent	<.01	.25	.10	3.6	2.88		
Plant Simulation Effluent	<.01	.20	.04	6.90	1.01		

Plant 8

	pH	*TS*	*DS*	Cr^{T}	Cr^{+6}	*Cu*	*Ni*
Plant Underflow (ASTM-A)	9.84	11,900	2,400	<0.1	<0.05	0.08	0.20
Plant Simulation Underflow (ASTM-A)	9.50	11,500	3,370	<0.1	<0.05	<0.05	0.10
Plant Simulation Underflow with Correction for Dilution				*	*	*	0.03
Plant Effluent***	9.16			0.22		1.09	
Plant Simulated Effluent***	9.5			0.88		0.79	0.55

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*Correction factor cannot be applied.
**After settling for 2.25 hours.
***Analysis was for dissolved metal rather than total metal in order to determine the effectiveness of treatment.

273 was effective at 2 mg/l and was throughout further studies.

TREATMENT STUDY

Test Plan

Treatment studies were conducted to determine the effect of treatment chemical and pH on the effluent quality and on the leachability of the sludges produced. The method utilized to achieve these goals was to take actual untreated electroplating wastewaters and treat them with three common precipitation chemicals: sodium hydroxide (NaOH), soda ash (Na_2CO_3), and lime (CaO). Tests were conducted with each of these chemicals on the wastewater with the pH adjusted to 8.5, and 10 (see Figure 1). A 15-liter portion of the wastewater was treated in a manner similar to the plant's treatment system except for the change in chemicals and pH (and the flocculant changes noted above) so that the plant could easily implement any recommended changes. Individual waste streams were mixed in the proper proportions. Appropriate retention times were allowed and after flocculation and settling the supernatant (overflow) was decanted and analyzed for its metal content. The remaining sludge layer (underflow) was then drawn off and filtered through a 0.45 micrometer filter. The filtrate was analyzed for its metal content. Washed and unwashed portions of the sludge cake were subjected to the EP and ASTM-A extractions. Due to the small amounts of sludge generated in some plants and to provide uniform results for comparison the sludges were subjected to the EP and ASTM-A extractions as follows.

A portion of the sludge cake (30 g) was washed by homogenizing the sludge in 100 ml of deionized water and mixing for 5 minutes. The washed sludge was then filtered through a 0.45 micrometer filter. This filtrate (wash filtrate) was analyzed for its metal content. This fraction reflected the amount of the metal associated with interstitial water which contributed to the leachability of the sludge. The unwashed and washed sludge cakes were then extracted identically by both the EP and ASTM-A extraction procedures.

The EP was performed using 5.0 g of filter cake and the ASTM-A extraction used 20.0 g of filter cake. The extracts from these extractions were analyzed for metals.

Analytical results from these laboratory tests were compared to each other and to the plant's samples to determine which combination of chemicals and pH resulted in the best performance based on effluent quality and sludge leaching characteristics.

Sludge Leachability

Leachability studies on washed and unwashed sludges were performed using the EP and ASTM-A extraction procedures. These extractions differ considerably in that the EP is conducted using an acidic (pH 5) extraction whereas the ASTM-A procedure is an extraction with deionized water.

The Cd, Zn and Cr levels in the ASTM-A extracts for Plant 2 washed and unwashed sludges followed the same trends as the washed filtrate and unwashed filtrate respectively. Chromium was well stabilized against leaching having values near or below its detection limit. The lowest leachability of metals was observed with CaO and NaOH treatment at pH 10. The lower levels of metal in the ASTM-A extracts appeared to be mainly due to a dilution of the interstitial water and not to additional leaching by the ASTM-A extraction. The EP extracts show much higher levels of leaching of these metals due to their increased solubilities at pH 5. Cadmium and Zn levels were high for both washed and unwashed sludges. They exhibited little variability with precipitation chemicals and showed minimal pH effects. The washed sludges leached significantly lower amounts of Cr. Unwashed samples showed a pH effect favoring pH 8.5. Precipitation by Na_2CO_3 resulted in a 10-fold increase in Cr leachability.

In Plant 3, Cd was readily leached in the EP extraction while negligible leaching occured in the ASTM-A extraction. This contrasted with the behavior of Cr. The low leachability of Cr in the EP extraction compared to the ASTM-A extraction may result from the reduction of Cr^{6+}, under the acidic conditions of the EP extraction.

The most stable sludge generated in Plant 4 experiments may be interpreted in terms of the leachability of Cu and Ni, the two predominate metals in the waste stream. Chromium leached less than 1.0 mg/l in both the ASTM-A and EP extractions. Lime at pH 10 produces the most favorable levels of metals under the EP extraction. There was much lower variability in these sludges under ASTM-A extraction conditions.

In Plant 6, the EP extract of the CaO precipitated sludge at pH 10 showed the lowest levels of Ni. The washed and unwashed sludges extracted by ASTM-A leached very little Ni. Chromium was best stabilized in CaO and NaOH sludges precipitated at pH 10 for the EP extraction while

Table 4
Results of Flocculation Study

Flocculating agent	Manufacturer	Optimum Concentration (mg/l.) Plant 2	3	4	6	7	8
Blank		poor	poor	poor	poor	poor	poor
Separan AP-273	Dow	poor	poor	1.0*	4.0	1.32*	2.0*
Magnifloc 836A	Cyanamid	2.0*	poor	poor	2.0		poor
L67OE	Calgon	poor	poor	poor	poor		poor
WT-3000	Calgon	8.0	0.5*	4.0	poor		4.0
Separade P-3	Benchmark	—	—	1.5(5)	—	—	—
Percol	Allied Colloids	—	—	—	2.0*(6)	—	—
Floc 306	EPEC	—	—	—	—	—	5.0(5)
Hercofloc	Hercules	—	—	—	—	(0.1)	—

* Indicates flocculating agent and concentration used for each plants treatment study.
( ) Indicates approximate concentration used in the plant.

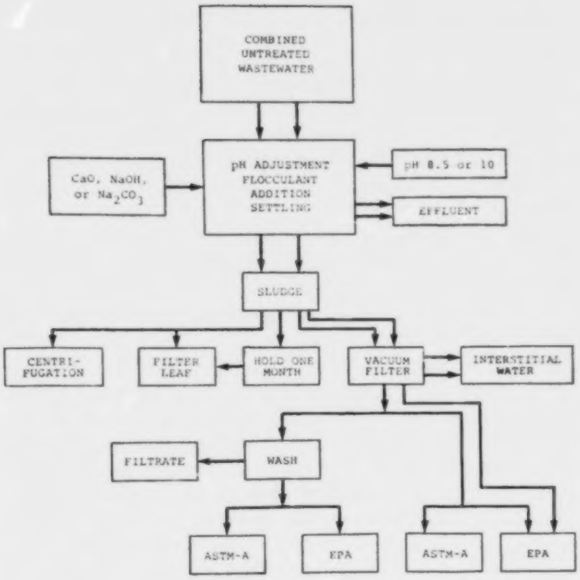

Fig. 1—Test Program and Analytical Plan.

pH 8.5 proved better for the ASTM-A extraction. The Cr extracted by ASTM-A or the EP extractions was below 5 mg/l for all treatments and considerably better for some treatments. It is interesting to note that the ASTM-A method leached chromium as hexavalent chromium although little or no Cr^{6+} was in the effluent or filtrates. It is unclear what caused this result. The trends through the treatment series for Cr(T) and Cr^{6+} are very similar which tends to corroborate this result.

Plant 8 treatment with Na_2CO_3 produced a floc with very poor settling characteristics. A significant amount of particulate matter was apparent in the partially cleared supernatant. This sludge cake also was very unstable toward leaching of metals by both the ASTM-A and EP extractions, especially at pH 10. Chromium and Cu levels in the EP extract of Na_2CO_3 precipitated sludges were exceptions and were by contrast the lowest for these metals in the treatment series.

CONCLUSIONS

Effluent Quality

Plant 2

Cr concentration was reduced to below the analytical test detection limit with NaOH and CaO_3 at pH 10.

Cd and Zn were also lowered by NaOH, CaO and Na_2CO_3 at pH 10.

Plant 3

The presence of Cr^{+6} presented problems in all of the simulation experiments. Cr^{+6} should have been chemically reduced in the laboratory studies before the chemical treatment.

The best Cd removal was achieved by CaO and NaOH at pH 10.

Plant 4

Ni, Cu and Cr were reduced by NaOH and CaO at pH 10. Cr levels were below the analytical detection limit.

Plant 6

Cr and Ni were reduced below the analytical detection limit by CaO and NaOH at pH 10.

Plant 8

No Cr^{+6} was found. Cr, Cu, and Ni were effectively removed with NaOH, and CaO at pH 8.5, 10.

Sludge Leachability

All plant sludges as initially tested by the EP test were hazardous.

Plant 2

All treatments failed to produce a nonhazardous sludge. CaO and NaOH at pH 10 produced nonhazardous leaches of Cr.

Plant 3

The sludges failed the EP test for Cd. Cr remained nonhazardous.

Plant 4, 6, 7

Made nonhazardous with all treatments.

Plant 8

No treatment conditions produced a nonhazardous sludge.

RECOMMENDATIONS

The following recommendations are based on observations made during the testing and engineering evaluations of the data.

- To determine whether or not the conclusions drawn from this test program are valid, it is recommended that the electroplating shops from this study adopt the optimum treatment chemical, pH, and flocculant and study the results in their effluent.
- Several more electroplating shops should have their treated wastewater studied to see if the two correlations generated from this study can, in fact, predict ASTM-A results from the quantities of Cd and Cr in the sludge filtrate.
- Owners and operators of electroplating shops should be informed as to the results of this study so that they may see that improvements can be made to any electroplating shop. More educational courses need to be given on wastewater chemistry, treatment, and control.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

Outlook For New Hazardous Waste Management Technology

Robert B. Pojasek, Ph.D.*

INTRODUCTION

In most cases, conforming to the proposed new effluent regulations issued by the U.S. Environmental Protection Agency (U.S. EPA) will bring about the production of more heavy metal-containing sludges in the Metal Finishing Industry. This comes at a time of strict regulation, also by the EPA, of sludge disposal. Gone are the days of cheap landfill disposal when $1.50 per ton was the going rate. Cost today often pushes the $100 per ton mark.

It is highly likely that there will be fewer landfills in the future and those which do exist will be tightly controlled. In California, the Governor has announced an outright ban on the disposal of "toxic metal" waste effective January, 1983. In the meantime, disposal fees and enforcement will be increased to promote early conformance to this ban. Other states have also taken moves to severely limit the amount of waste that is landfilled. The Ontario Waste Management Corporation has gone on record signifying that only "treated" wastes will be landfilled in the facilities it seeks to develop.

Numerous publications and patents have appeared describing technology effective for treating metal finishing sludges and assorted other solids. At this time, very little of this technology has gained wide acceptance for various reasons, including inadequate promotion, limited adaptability, and unfavorable economics. This paper will examine some of the technological means that may be utilized to handle the solid residuals from a metal finishing plant. Special emphasis will be placed on those residuals which are determined to be hazardous under the federal Resource Conservation and Recovery Act (RCRA) or any other set of state regulations.

Waste Minimization

The first line of defense is to minimize waste production to the maximum extent possible. Many EPA publications promote this concept with helpful suggestions. What the metal finishing shop needs is an organized program to consider and implement these plans.

A useful progam can be individually designed around the following key steps:

- First, carry out a materials balance for water, metals and other chemicals used in the operation;
- From the materials balance, reduce consumption of water and chemical usage where this is indicated and incorporate simple process modifications which would enhance the potential for recovery of valuable constituents;
- Segregate the process of effluents as far as possible to facilitate the removal of metals; and
- Identify possible outlets for recovered materials and provide any necessary process for producing the wastes in an economically acceptable form (e.g., delisting treatment or simple volume reduction).

If this program is designed just for waste quantity reduction a general approach to conduct the steps described above is as follows:

- Identify all wastes;
- Prioritize all wastes according to costs;
- Develop waste quantity and/or elimination plans for each waste;
- Assess the economic and technical feasibility of these plans; and
- Implement those plans that are shown to be cost effective.

It is often helpful to seek the assistance of a qualified consultant. Independence from day-to-day operations and familiarity with other successful operations can be most useful to your staff in conducting your own program.

The American Electroplaters' Society, Inc. can assist its member firms by keeping up-to-date on the activities of various groups looking for means to help achieve waste minimization. These groups include EPA's Hazardous Waste Elimination Research Institute, United Nations' Program for low-waste and non-waste technology, Ontario Waste Management Corporation's Waste Reduction Opportunities Study, and the California Office of Appropriate Technology's Alternative Waste Management Technologies Study, to name but a few. This information must be made readily available and periodically updated.

In-Plant Waste Treatment

Many metal finishing plants are small operations. While they can assist themselves by altering housekeeping practices which will result in lower volumes of waste produced, it has been argued that they cannot utilize in-plant technology because of the relatively high capital costs of the equipment and retrofitting. This may be true for some operations, especially if recovery value or reduced disposal costs do not significantly reduce the return on investment period. Fortunately, this perceived lack of need has not completely prevented the introduction of new technology applications.

Successful water use reduction programs have dramatically altered the characteristics of the wastewater streams. Low volume streams with higher metal concentrations are more amenable to electrochemical treatment. Because these units can be utilized close to the process line, segregation of metals in the input stream is possible, thus enhancing the prospects for metal recovery.

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Extended surface electrodes have been developed to prevent fouling. The amount of waste streams requiring treatment has been further reduced at some locations by using advancing membrane technology to regenerate process solutions until the impurity levels reach a point where the above treatment is required.

There has been an increasing application of sodium borohydride for chemical treatment of these waste streams while enhancing the metal recovery potential of the product. Perhaps other chemical treatment techniques can be developed for this application. Finally, this waste stream can be treated in a more or less classical metal precipitation manner with dewatering. Metal recovery can be handled off-site if the waste streams are not mixed prior to treatment.

Centralized Waste Treatment

The EPA has actively tested and promoted the concept of centralized treatment of liquid metal finishing wastes. This concept offers favorable economies-of-scale to the small shop operations. There has been an increasing number of these plants operating on a commercial basis. Because many of them have located in industrialized areas and have refrained from disposing any residues on-site, they have not had the overwhelming difficulties in siting their facilities. A number of companies in the business have received formal exclusions (i.e., delistings) from EPA's RCRA regulations. This enables them to handle plant residues as a non-hazardous material. Those seeking to delist a material, however, will have the burden of proof. If a waste is to be delisted, it must be tested for each hazardous characteristic that it was listed for and it must perform favorably on all the tests. At least one operation which has obtained such an exclusion plans to market the material as sanitary landfill covering because of its relatively low permeability when properly placed on the landfill.

Most of these centralized facilities are using classical and chemical treatment processes (e.g., precipitation, oxidation, reduction, dewatering, etc.) on mixed influent streams. The EPA exclusions offer operating incentives by dramatically lowering the residuals disposal costs. These facilities should become the focus of research, development and demonstration activities for improving recovery and reuse opportunities. However, this is not happening. In order to realize this opportunity, the facility would have to encourage its customers to segregate waste streams. A program to handle and treat these segregated streams must be established and maintained.

When recovery of the waste stream is not being practiced or when the residuals of the recovery operations are deemed to be hazardous, solidification technology is sometimes utilized to enable delisting. Many articles have been written on the use of solidification. Some references are provided at the conclusion of this paper. In spite of the articles, a great number of "old wives tales" have been perpetuated—many of them in EPA reports. The answers to some of these falsehoods are as follows:

- There are over 40 commercially available processes with many more generic processes being utilized;
- Some volume reduction systems are available to actually reduce the bulk of the solidified waste;
- Some forms of strict encapsulation (especially with thermo-plastics) are often more effective than chemical fixation processes, especially for soluble anions; and
- There are a number of processes to solidify organic wastes with several quick-line processes leading the way.

Reduction of secure landfill capacity should provide incentives for increased use of solidification when delisting and uses for the product can be found. However, a number of delistings in the metal finishing area have been obtained without solidification. Increased recycling and reuse programs will also provide disincentives to the further use of solidification.

Waste Treatment Research and Development

It has been difficult to devote a lot of space in this article to describing new technologies for use in handling solid wastes from the Metal Finishing Industry—there have been very few. EPA research and development budgets are being trimmed. The hazardous waste research and development institutes which have been established by EPA are not considering metal finishing wastes as a priority item. EPA has spent technical assistance contract funds to assist states with concentrations of metal finishers in dealing with this industry in its regulatory programs. However, these activities have not been well-coordinated and their reports have not been well-distributed. The metal finishing industry has always been effective in working with the EPA Office of Research and Development to develop new means of wastewater treatment. It is time to dig in and complete the task by funding, to the extent needed, directed research and development to maximize recovery potential of the solid waste streams.

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Segregated Neutralization for Treatment of Concentrated Aluminum Finishing Wastes

F. Michael Saunders, Mesut Sezgin, Jesus M. Medero[*]

INTRODUCTION

Aluminum products are widely used in many industries including construction, electrical, automotive, and food and household good manufacturing industries. In the United States approximately 6×10^6 Mg (metric tons) of aluminum are used annually for domestic consumption.[1] Of the total consumption, approximately 90% is converted to various forms such as sheet, bar and wire, and subjected to a wide variety of surface-treatment and finishing processes in well over 600 major production facilities.[2]

With the emphasis of this study on water quality control, it is appropriate to consider the nature of the finishing processes used and the waste volumes produced in the industry. In the aluminum finishing industry numerous physical and chemical treatments (e.g., buffing, cleaning, deoxidizing, painting and anodizing) are used to improve surface appearance, durability, and adhesion properties. Physical surface treatments conventionally utilized by the industry include mechanical polishing, buffing and brushing. The wastes associated with these finishing processes are solid wastes and oil-bound suspensions which can be effectively recycled or treated and disposed. Chemical finishing processes include chemical and electrochemical etching and polishing, chemical milling, painting, and anodizing. The wastewaters associated with these finishing processes consist of large volumes of rinse waters, smaller volumes of chemical spills, and spent or contaminated finishing solutions and suspensions.

Wastewater Characteristics

Wastewaters from aluminum finishing processes contain a variety of inorganic and organic contaminants resulting from finishing solutions and aluminum products being finished. These contaminants are discharged in rinse water discharges and dragout and spills of finishing solutions. They include aluminum, and other substances such as arsenic, barium, cadmium, chromium, copper, iron, manganese, magnesium, mercury, nickel, selenium, silver, and silica.[3] Spills of cleaning solutions and rinse waters following cleaning contain sodium, carbonate forms, phosphates, silicates, chelating agents and synthetic detergents or soaps.[4] In the etching step, which is utilized to remove surface oxides, sub-surface detritus and grease, spent etch wastes are generated which contain high levels of aluminum, e.g., 10-75 g/L. In addition, spent etch solutions may contain silicates, fluorides, nitrates, carbonates, chromates, wetting agents, copper, zinc, and chromium. Rinse waters following the etching step also contain these contaminants, but at lower concentrations. Desmutting solutions are used in the removal of smudge films formed during etching and are the primary solutions contributing to effluent nitrogen in the form of nitrates.

In the anodizing step, a film of aluminum oxide is formed on aluminum surfaces for decorative and protective purposes using anodizing solutions composed primarily of acids, such as sulfuric, chromic, phosphoric, and oxalic acids. During anodizing, aluminum and other alloy metals such as copper, zinc, arsenic, lead and iron are dissolved. Aluminum concentrations in anodizing solutions may range from 0.5-20 g/L. However, when aluninum concentrations exceed prescribed limits, the anodizing solution is regenerated using an ion-exchange resin or is discharged. Regenerant acids and spent etch solutions are discharged to a wastewater treatment system in the plant.

Coloring is applied on aluminum surfaces using organic dyes, certain inorganic pigments, and electrolytically-deposited metals.[4] For this purpose, solutions containing organic dyes, nickel, cobalt, tin, selenium, vanadium, cadmium, copper, iron, magnesium, lead, chromium, acetate, cyanide, and sulfite have been used. Sealing is applied to modify the characteristics of the anodic coating. A number of solutions have been used for sealing purposes including distilled water with buffers, nickel acetate, salts of aluminum, cobalt, zinc, copper, lead, chromium, and sodium or potassium dichromate, alkali-metal silicates, and waxes.

Water consumption rates in aluminum finishing plants are in the range of 25 to 67 L/kg of aluminum finished.[5] High water use rates are due to increased dragout of finishing solutions which result in high rinse water requirements. In addition, the formation of viscous liquid films on products being finished requires large volumes of rinse water for their removal.

Aluminum finishing wastewaters, therefore, contain high levels of dissolved solids (e.g., 1.5-6.0 g/L for anodizing and painting wastes, and up to 315 g/L for etch plant wastes) which limit the reuse potential for these wastewaters. A survey of aluminum finishing plants indicated that 0.9 to 2.4% of the mass of aluminum extruded and finished in extrusion/anodizing plants was dissolved and discharged to waste.[6] Wastewaters also contain organic materials such as detergents, etch sequestrants, spent dye, organic acids, and acetate in the range of 30-100 mg TOC/L.[6]

Wastewater Treatment

Conventional treatment of aluminum finishing wastewaters is achieved through mixing all rinse waters, spent process solutions, and process spills in a multi-stage neutralization system. Highly concentrated spent etch and anodizing solutions are usually collected and stored for use in controlling wastewater pH in the neutralization system. Therefore, rinse waters and spills with relatively low levels of dissolved aluminum are typically neutralized with highly

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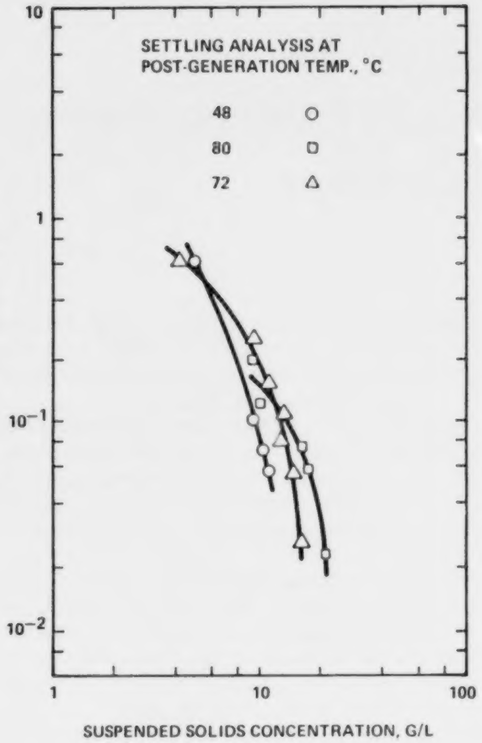

Fig. 1—Effect of temperature on settling characteristics of sludges generated at elevated temperatures and neutral pH.

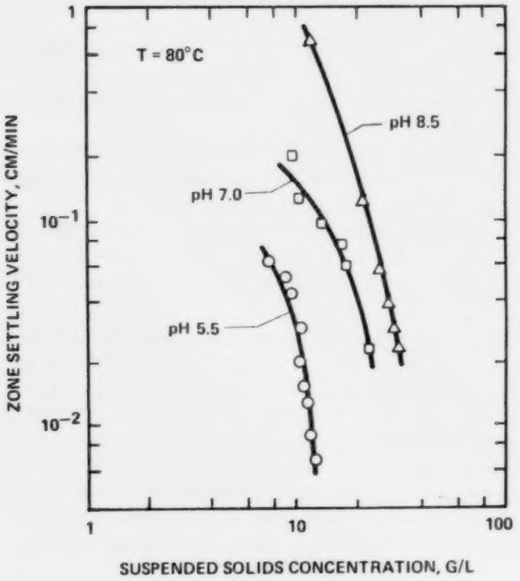

Fig. 2—Effect of pH on settling characteristics of sludges generated at 80° C.

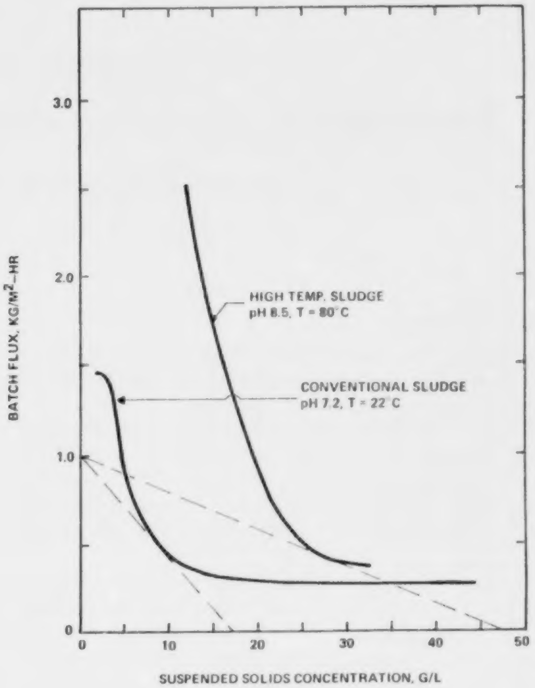

Fig. 3—Batch flux curves for sludges generated by conventional and segregated (high temperature) neutralization of aluminum finishing wastes.

concentrated acidic and alkaline suspensions containing high levels of waste aluminum. When combined wastewaters are neutralized to pH values ranging from 6 to 8, aluminum is precipitated as an aluminum hydroxide. Wastewaters from painting processes utilizing chromate solutions are generally pretreated for chromate reduction. Hexavalent chrome is reduced to trivalent chrome, with reducing agents such as ferrous iron, sulfur dioxide or sulfite, and precipitated as a hydroxide at alkaline pH values.[7]

Neutralized anodizing and painting wastewaters are typically polymer-conditioned and gravity settled. Clarified wastewater is either discharged to a receiving water or sewerage system for additional treatment. Thickened sludges are either discharged to sludge lagoons for further thickening and consolidation or conditioned, dewatered, and disposed of on land.

The results of a survey conducted on aluminum finishing plants indicated that clarifier underflow suspensions had an average suspended solids concentration of 22 g/L with a range of 0.1 to 50 g/L.[6] With the use of mechanical dewatering systems, sludge concentration was further increased to a range of 1-20% with an average value of 16.5%. If it is assumed that the sludge solids contained only aluminum hydroxide (A1(OH)^{3}), the average survey value of 16.5% represented 17.5 kg of wet sludge for each kg of aluminum precipitated. It was further reported that 0.8 to 2.4% of finished aluminum is dissolved during finishing.[6] This would correspond to the production of 0.16 to 0.42 kg wet sludge (at 16.5% solids) for each kg of aluminum finished. If a sludge solids concentration lower than 16.5% is encountered, the relative quantity of dewatered sludge for disposal would approach finished aluminum production levels.

To reduce the volume of sludge handled, other treatment techniques have been investigated. One of these treatment methods involves the segregation of spent finishing solution from dilute waste solutions (such as rinse waters) and neutralization in a separate reactor. By this treatment alternative, sludge could be concentrated to 20% solids, instead of 2% solids as observed with conventional treatment

Table 1
Characteristics of Acidic Anodize and Caustic Etch Suspensions

Parameter	*Spent Anodize Suspension*	*Spent Etch Suspension Sample No.* 1	2	3	4	5
pH	0.55	13.5	13.5	13.7	13.3	13.8
Temperature, °C	21	50	50	50	50	50
Aluminum, g Al^{+3}/L	7.50	51.0	45.8	38.2	35.6	41.3
Alkalinity, g/L as $CaCO_3$	—	405	454	489	454	528
Acidity, g/L as $CaCO^3$	340	—	—	—	—	—
Color	light brown	dark green				

Table 2
Sludge Generation and Dewatering Analysis Conditions For the Five Experimental Runs

Sludge Generation			**Dewatering Test Variables**								
		Hydraulic Retention Time	*Specific Resistance Test*			*Filter Yield Test*				*CST Test*	
Run	*pH*	*(min)*	*Temperature*	*Vacuum*	*SS*	*Temperature*	*Vacuum*	*SS*	*Form Time*	*Temperature*	*SS*
1	8.5	10.2	X	X	X	X	X	X	-	X	X
2	7.0	9.2	-	X	X	-	X	X	X	-	X
3	5.5	9.2	-	X	X	-	X	X	X	-	X
4	10.0	10.2	-	X	X	-	X	X	X	-	X
5	8.5	10.2	-	-	X	-	-	X	X	-	X

X indicates that the parameter was varied to determine effects on dewatering properties of sludge while all the other parameters were kept constant.

SS = Suspended Solids

Table 4
Impact of a Segregated Treatment of Spent Process Wastewaters at Plant A-3 on Sludge Dewatering Characteristics

Sludge Generation pH	*Sludge Generation Temperature °C*	*Specific Resistance R(10^{10} m/kg)* *FSS*[1]	*R*	*Filter Yield, F(kg/m² s × 10³)* *FSS*	*F*	*Cake Solids, %*	*CST (s)* *FSS*	*CST*
Segregated Neutralization								
5.5	80	12.8 - 157.5	22.5 - 31.0	35.0	2.8	34.0	35.0	63.0
7.0	80	16.4 - 151.1	2.33 - 3.18	35.0	9.6	34.6	35.0	25.0
8.5[2]	80	20.8 - 157.8	1.33 - 2.95	35.0	6.2	42.2	35.0	25.0
10.0	80	25.4 - 256.3	0.34 - 0.87	35.0	0.78	52.8	35.0	25.0
Conventional Neuralization								
7.0[3]	25	3.4 - 36.1	28 - 38	3.4 - 36.1	0.70 - 5.71	8.5 - 9.2	3.4 - 36.1	18.1 - 53.7

[1] Feed suspended solids concentration, g/l
[2] Filter yield data from run #5
[3] Conventional sludges from Plant A-3

Table 5
Impact of a Segregated Treatment of Spent Process Wastewaters at Plant A-3 on Required Vacuum Filter Area and Mass of Sludge for Disposal

Generation pH	*Generation Temperature °C*	*Feed Suspended Solids Concentration g/l*	*Filter Yield kg/m²-s*	*Cake Solids Concentration %*	*Filter Area Required m²*	*Mass of Sludge for Disposal kg/day*
5.5	80	150	1.10×10^{-2}	34.2	11.41	7,924
7.0	80	150	4.00×10^{-2}	34.8	3.14	7,787
8.5	80	150	3.40×10^{-2}	40.0	3.69	6,775
10.0	80	150	6.00×10^{-1}	46.7	20.91	5,803
7.0	25	-	5.71×10^{-1}	9.2	21.97	29,457

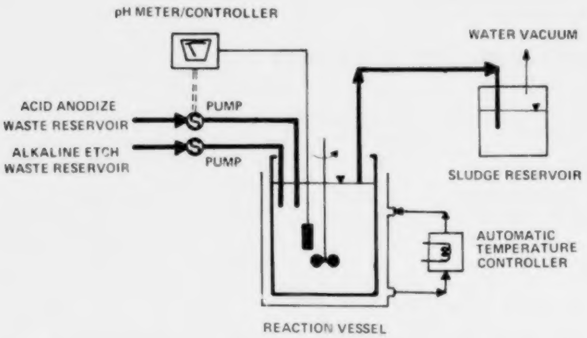
pH METER/CONTROLLER
WATER VACUUM
ACID ANODIZE WASTE RESERVOIR
PUMP
ALKALINE ETCH WASTE RESERVOIR
PUMP
SLUDGE RESERVOIR
AUTOMATIC TEMPERATURE CONTROLLER
REACTION VESSEL

Fig. 4—Schematic diagram of laboratory-scale neutralization systems.

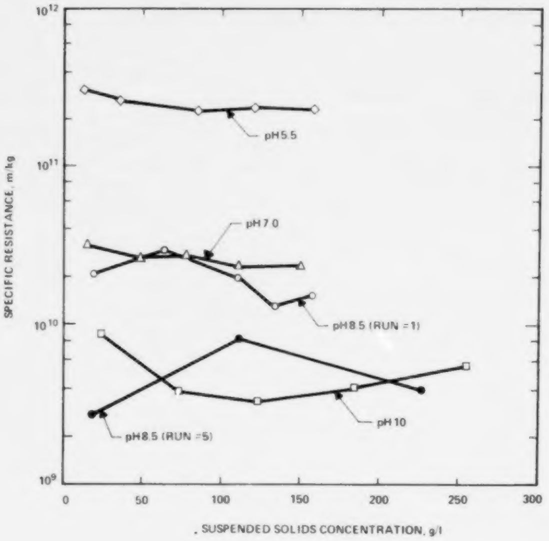

Fig. 5—Variation of specific resistance with suspended solids concentration at room temperature for sludges generated at 80°C and at various pH values.

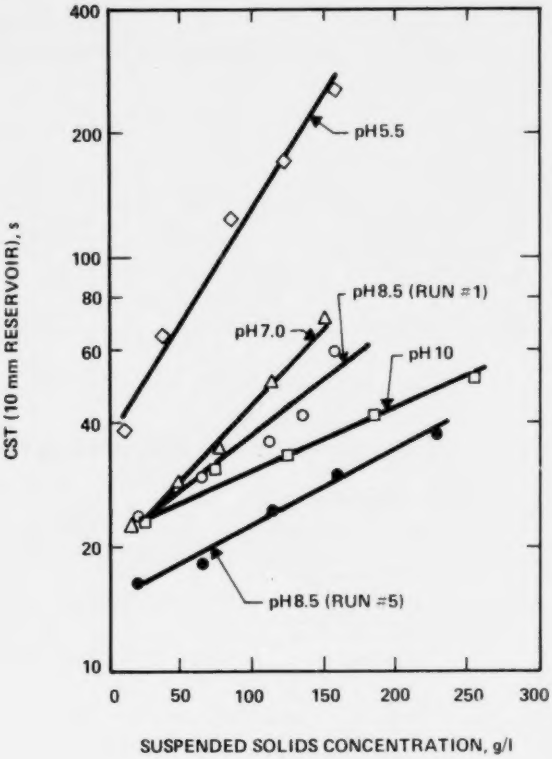

Fig. 6—Variation of capillary suction time (CST) with suspended solids concentration at room temperature for sludges generated at 80°C and at various pH values.

technologies.[8] Ledfore[9] reviewed solid-liquid separations in the treatment of metal finishing wastes and indicated that the neutralization of concentrated acidic wastes was shown to result in improved handling and filterability when neutralized or aged at 71-82°C. The sludge moisture content following dewatering was also significantly reduced. Furthermore, pH adjustment of the neutralized liquor was found to affect the settling rate of sludges.

An industrial survey conducted by Ramirez[10] indicated that 80 to 85% of the mass of wastewater aluminum at an anodizing plant was contained in concentrated spent etch and anodizing wastewaters.[6] Therefore, segregated neutralization of these wastes would reduce the solids loading on a conventional treatment system. More importantly, depending upon pH and temperature of neutralization, a sludge with much improved settling and dewatering characteristics would be produced, resulting in major reductions in the volume of wet sludge to be disposed.

The objective of the study reported herein was to evaluate the effect of neutralization pH of concentrated etch and anodization wastes on dewatering characteristics of sludge generated at 80°C. Other objectives included determination of the effects of sludge viscosity, suspended solids concentration, form time and applied vacuum on the dewatering and handling characteristics of the sludges formed.

EXPERIMENTAL METHODS AND MATERIALS

Etch and anodize wastewater samples from an aluminum finishing industry were collected and mixed in a continuous flow bench-scale neutralization system. Aluminum hydroxide suspensions generated at various pH values were examined for their dewatering properties under various experimental conditions including temperature, vacuum and form time.

The continuous flow neutralization system consisted of a 0.8-L reaction vessel stirred at 150 rpm with a single-paddle metal stirrer as presented in Figure 4. The contents of the reaction vessel were maintained at a constant temperature of 80°C with an automatic temperature controller which provided recirculation of the hot/cold distilled water through an external water jacket.

Peristaltic pumps equipped with flow rate controllers were used to pump etch and anodize wastes to the reaction vessel. During sludge generation, the anodize waste flow was kept constant while the etch waste flow was regulated with an automatic pH controller to maintain the pH of a neutralized suspension at required values. Influent flow rates were

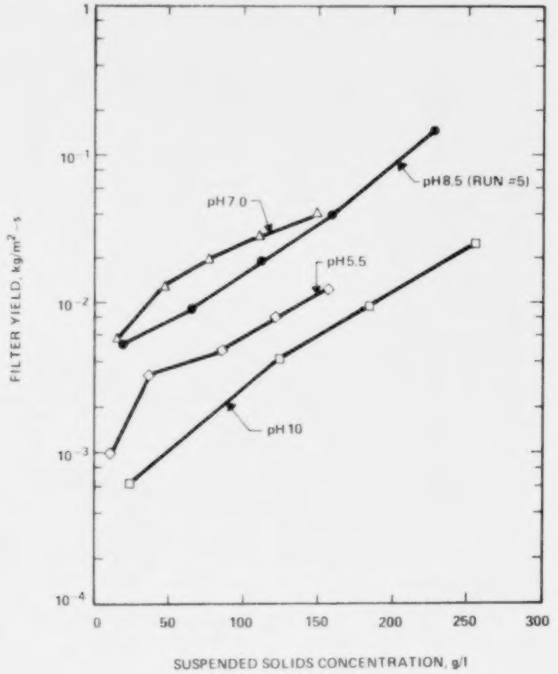

Fig. 7—Variation of filter yield with suspended solids concentration at room temperature for sludges generated at 80 C and at various pH values.

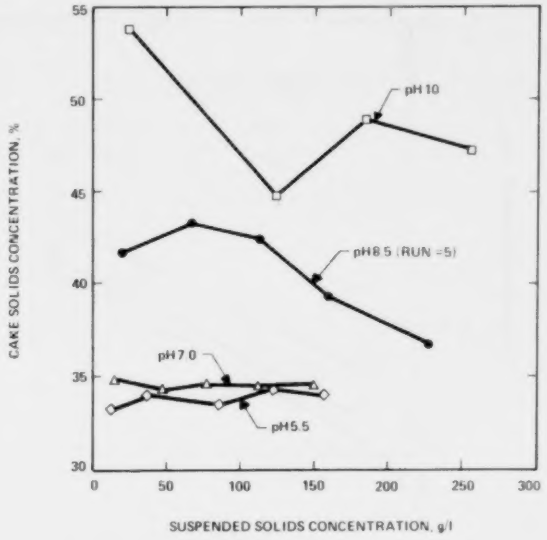

Fig. 8—Effect of feed suspended solids concentration on cake solids concentration at room temperature for sludges generated at 80 C and at various pH values.

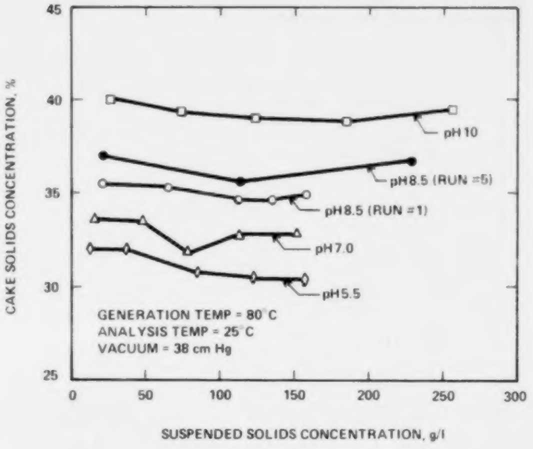

Fig. 9—Variation of cake solids concentration with suspended solids concentration at various pH levels in specific resistance tests.

adjusted to maintain hydraulic retention times of approximately 10 minutes in all runs. Neutralized aluminum hydroxide suspensions were removed from the reactor by vacuum and transferred to a glass container held at the temperature of generation in a constant temperature water bath.

Sulfuric acid anodize and caustic etch suspensions were obtained from a major regional aluminum finishing plant. The characteristics of these wastes are indicated in Table 1. Since changes in waste characteristics after prolonged storage were observed with spent etch suspensions, fresh etch samples were used for each experimental run. For this reason, Table 1 contains data for five spent etch samples used during the study. Measurements of pH, temperature, alkalinity and acidity were made in accordance to the methods described in *Standard Methods for the Examination of Water and Wastewater*.[12]

Dewatering tests were conducted with aluminum hydroxide suspensions using a Buchner funnel, and filter leaf and Capillary Suction Time (CST) apparati. Prior to dewatering tests, aluminum hydroxide sludges collected in a 20-L glass container were allowed to settle and a series of dilutions in the range of 10 to 100% volume of the settled sludge were prepared using clarified supernatant liquid.

Sludge specific resistance values were measured to evaluate sludge dewatering ability.[13] Filtration temperature, and vacuum and feed suspended solids concentrations were varied to determine the effect of these parameters on dewaterability of sludges generated at different pH values. Filter leaf test measurements were used to determine filter yields in accordance with the method described by O'Connor.[10,13] Similarly, the effects of filtration temperature and vacuum, feed suspended solids concentration and form time on filter yield were evaluated. CST measurements were conducted using a type 92/1 CST appartus and a hollow, cylindrical, metal reservoir of 10 mm diameter. The effects of temperature and suspended solids concentration on dewaterability of sludges were determined.

To investigate the effect of neutralization temperature and pH on settling characteristics of sludges produced by segregated neutralization, extensive studies were conducted by Saunders *et. al.*[11] Waste etch suspensions (i.e., 5.5N NaOH at 2.4 M Al) and anodize suspensions (8N H_2SO_4 at 0.6 M Al) were neutralized at pH values ranging from 5.5 to 8 and temperatures from 65 to 90°C. As indicated in Figure 1, temperature variations of 48 to 72°C (for suspensions generated at temperatures of 65 to 90°C and a pH of 7) did not significantly affect zone settling properties. However, sludge suspensions generated and analyzed at 80°C indicated marked improvement in sludge thickening characteristics with increasing pH values, as indicated in Figure 2. A comparison of batch flux settling data, for a suspension generated at pH 7 and 80°C using segregated neutralization with a conventional suspension generated at neutral pH values and ambient temperatures, indicated that

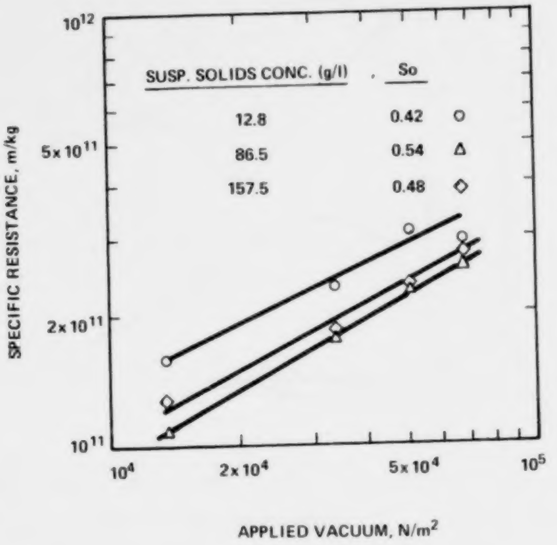

Fig. 10—Evaluation of compressibility coefficient, S_o, at various suspended solids concentrations for suspension generated at a pH of 5.5 and a temperature of 80° in experimental run 3.

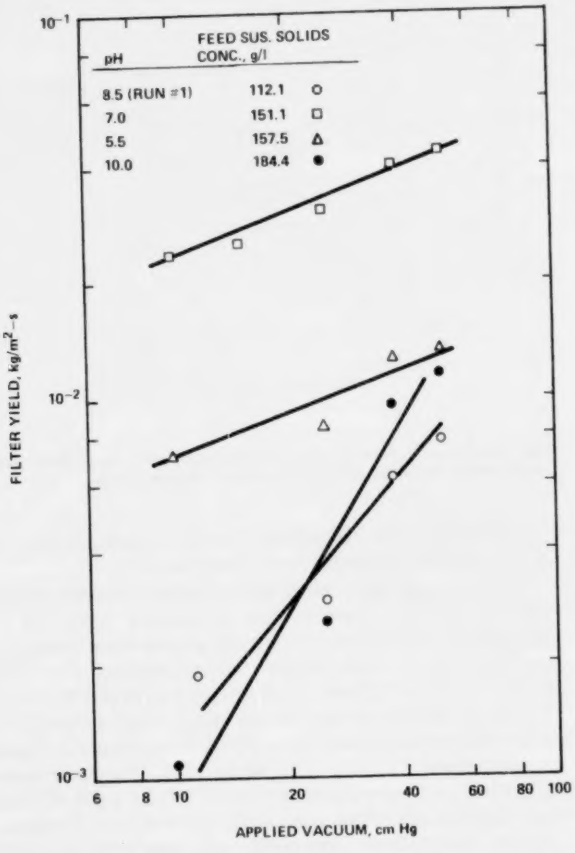

Fig. 11—Variation of filter yield with form vacuum for sludges generated at different pH levels.

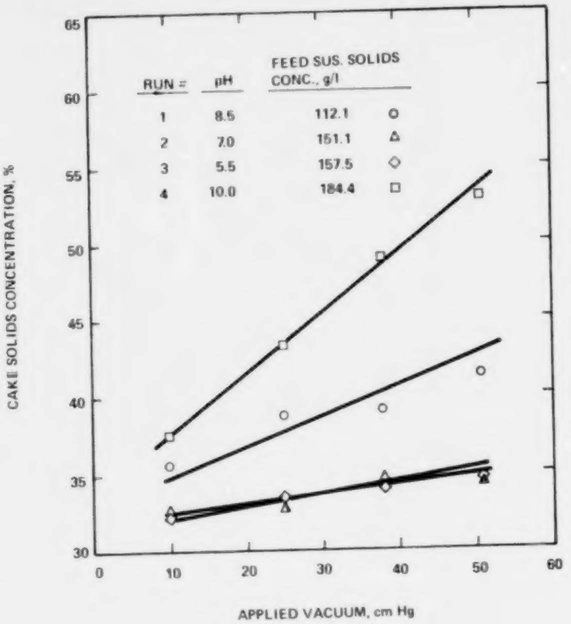

Fig. 12—Effect of applied vacuum pressure on cake solids concentration at room temperature for sludges generated at 80 C and at various pH values.

an approximate 3-fold reduction in sludge volume could be achieved at a solids flux loading of 1 kg/m²-h, as shown in Figure 3. Segregated neutralization therefore resulted in the production of a suspension which thickened much better than those generated using conventional neutralization.

RESULTS AND DISCUSSION

Five experiments were performed to determine the effect of neutralization pH on the dewatering characteristics of aluminum hydroxide sludges generated at 80°C. For each run, or neutralization pH, the dewatering properties of the sludges were measured under a variety of test conditions as given in Table 2.

Sludge Dewaterability at Various pH Values

The relationships between specific resistance and suspended solids concentration at various pH levels are presented in Figure 5. Because of random variations in specific resistance with suspended solids concentration, specific resistance did not appear to be affected by suspended solids concentration. There was a strong indication that specific resistance decreased with increasing pH values. For example, at pH 5.5, the specific resistance was approximately 2.50×10^{11} m/kg. When the pH was increased to 7.0 and 8.5, the specific resistance decreased to 2.7×10^{10} and 2.0×10^{10} m/kg, respectively. A further increase in pH to 10 resulted in a decrease in specific resistance to an average value of 5.1×10^9 m/kg. A second experiment for a sludge generated at pH 8.5 (Run #5) also resulted in a specific resistance of 5.1×10^9 m/kg. This may be attributed to several reasons. At this low level ($\approx 5 \times 10^9$ m/kg) it is extremely difficult to measure specific resistance due to rapid dewatering rates. More importantly, fresh etch waste was collected each time an experiment was conducted and this may have contributed to the formation of sludges with differing properties. Nevertheless, the effect of pH on specific resistance followed a pattern similar to that observed by Ramirez[10] for settling properties.

Variations in CST with suspended solids concentration and at various pH values are shown in Figure 6. CST values were observed to increase with suspended solids

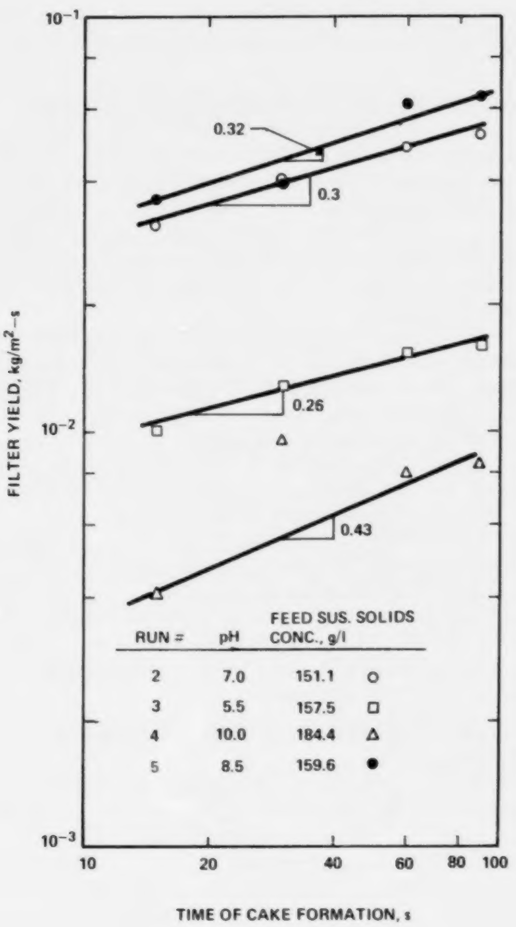

Fig. 13—Filter yield vs time of cake formation.

concentration and decrease with increasing pH. As observed with specific resistance data at pH 8.5 (Runs #5 and #1), lower CST values also were observed at pH 8.5 (Run #1). However, both runs resulted in similar CST values per unit weight of solids.

The relationships between filter yield and feed suspended solids at various pH levels are presented in Figure 7. No relationship is given for the sludge in Run #1 because the filter yield was determined at a vacuum of 51 cm of Hg instead of 38 cm of Hg used at other runs. It is apparent that an increase in pH from 5.5 to 7 resulted in an increase in filter yield. As indicated previously, specific resistance and CST of these sludges were both observed to decrease with sludge generation pH, indicating sludge filtrability was improved by increasing generation pH. From these observations, it would be predicted that filter yield should have increased with increasing pH. However, this was not the case with the results presented in Figure 7. Filter yield generally increased with increasing pH except for the sample generated at pH 10, which was contrary to indications from CST and specific resistance data. Variations in filter media used for filter leaf and specific resistance measurements were shown to have no effect on the dewatering trends. Factors affecting pickup of sludge particles in the up-flow filter leaf test, as opposed to development of a sludge cake with down-flow in the specific resistance test, were considered to have major impact on the variation from the trend of improving dewaterability with pH.

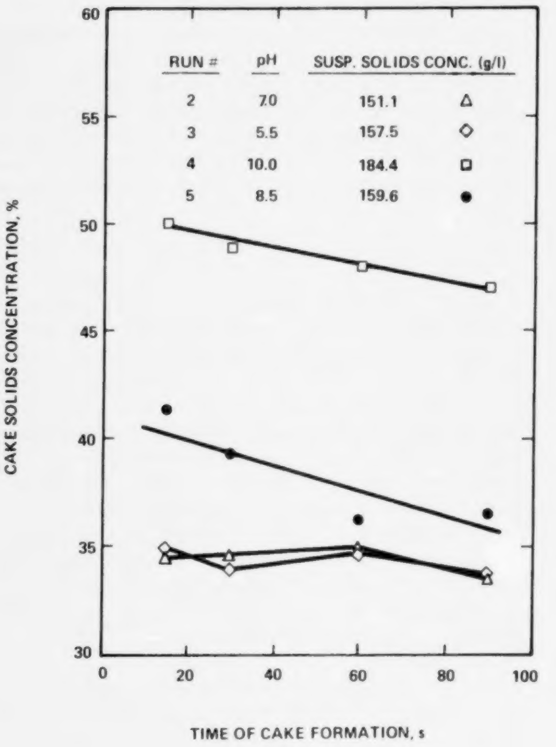

Fig. 14—Effect of time of cake formation on cake solids concentration at room temperature for sludges generated at 80°C and at various pH values.

In Figure 8, the effect of feed suspended solids concentration on cake solids concentration at various pH levels is presented for the filter leaf tests. For sludges generated at pH 5.5 and 7.0, cake solids concentrations are relatively constant with average values of 33.8% and 34.6%, respectively. Whereas, cake solids concentrations decreased with increasing suspended solids for the sludges generated at pH 8.5 and 10. This indicated that at the onset of the filtration process, particles picked up on the surface of the filter leaf formed a layer of low porosity. This layer lowered the passage of liquid coming out from the subsequent layer simultaneously formed in the course of filtration. Because of the higher resistance exerted by the first layer, the pressure at the interface of this layer and liquid was greatly reduced. Therefore, because of the lower pressure at the surface the next layers would be thin (e.g., lower filter yields) and have higher moisture content, as shown in Figure 8 with sludges generated at pH 8.5 to 10. However, in specific resistance experiments, cake solids concentrations were fairly constant with increasing suspended solids concentration at all pH levels (Figure 9). This observation was an indication of the gradual decrease of pressure through the cake rather than a sharp decrease in the first layers of the sludge in the filter leaf test experiment. The possible explanation of variations in behavior of the sludge in these two tests may be that there was preferential pick-up of small-sized particles in the filter leaf test experiments, whereas this did not occur for specific resistance experiments. The implication of these findings is that since the filter leaf test closely approximated the conditions present in vacuum filtration of sludges, predictions made about filter yields of vacuum filters based on the specific resistance experiments may not be accurate, especially for sludges in the low specific resistance values.

Vacuum Effects on Dewaterability

The effect of applied vacuum on specific resistance of sludges was examined at various levels. A typical relationship between specific resistance and vacuum pressure at various suspended solids concentrations is presented in Figure 10. When plotted on logarithmic coordinates, the relationship can be expressed by a linear relationship and be presented by the following expression:

$$r = r'(P)^{s_o} \qquad (1)$$

in which r = specific resistance; $r^{\prime}$ = cake constant; P = applied vacuum; and s_o = compressibility constant. The compressibility constant, s_o, was determined from the slope of the linear relationship and indicates the relative compressibility of a sludge. When s_o is zero, the sludge is incompressible and increasing values of s_o indicate increasing compressibility of a sludge. As apparent from the results, suspended solids concentration did not affect the compressibility constant for the sludges. Therefore average values of the compressibility constant were assumed to be representative for each sludge. Average values of the constants for various pH levels are presented in Table 3. The compressibility of sludges decreased with increasing pH which was consistent with the results of specific resistance experiments.

Variation of filter yield with applied vacuum for sludges generated at various pH levels is presented in Figure 11. When plotted on a logarithmic scale, the relationships followed a linear relationship which was consistent with the theoretical yield expression:

$$Y = \left[\frac{2Pwk}{\mu r \theta_c}\right]^{1/2} \qquad (2)$$

in which Y = filter yield; P = applied vacuum; w = dry solids deposited per unit volume of filtrate; k = form time fraction; μ = viscosity; r = specific resistance; and θ_c = total cycle time. In equation 2, k, μ and θ_c are constants when only applied vacuum is varied. In addition, w may be assumed to be constant and r varies with applied vacuum when the cake is compressible. Therefore, equation 2 may be combined with equation 1 as follows:

$$Y = A\ P^{(1-S_o)/2}$$

$$\text{where } A = \left[\frac{2wk}{\mu r' \theta_c}\right]^{1/2} \qquad (3)$$

A logarithmic plot of equation 3 results in a linear relationship with a slope of (1-s)/2. From Figure 11, as pH increased, the slope of the curves increased indicating that the compressibility constants decreased, which supported the previous observation that compressibility constants decreased with increasing pH levels. Furthermore, at a similar feed suspended solids concentration an increase in pH from 5.5 to 7 yielded an increase in filter yield. Further increase in pH to 10 resulted in lower filter values even though higher feed suspended solids concentrations were utilized.

Variations of cake solids concentration with applied vacuum are presented in Figure 12. For each sludge, cake solids concentration was observed to increase linearly with applied vacuum. Since cake solids concentration is an indication of the sludge volume which must be disposed of, the benefit of increasing applied vacuum to increase cake solids concentration should be weighed against the increases in capital and operational costs for dewatering, i.e., decreased filter yields.

Effect of Time of Cake Formation on Filter Yield

The variation of filter yield with the time of cake formation is presented in Figure 13. The data were collected at constant feed suspended solids (FSS) concentrations for various generation-pH levels. The slopes of the linear plots ranged from 0.26 to 0.43 which indicated that filter medium resistance was not significant and was consistent with the previous conclusion of the presence of insignificant filter medium resistance.

At any cake formation time, filter yield was observed to increase and subsequently decrease with increasing pH. A similar pattern with regard to the effect of pH on filter yield was observed with numerous feed suspended solids concentrations as shown in Figure 7.

Relationships between cake solids concentration and the time of cake formation are presented in Figure 14. While the sludges generated at pH 5.5 to 7.0 exhibited constant solids concentration with varying time of cake formation, the cake solids concentration for the sludges generated at pH 8.5 to 10 decreased. As previously discussed, initial sludge layers may have formed an impervious cake with fast-filtering sludges thereby lowering the filtration rate of subsequent layers and resulting in decreasing cake solids concentration as the number of layers increased.

ENGINEERING IMPLICATIONS OF SEGREGATED NEUTRALIZATION

To assess the impact of the segregated neutralization of spent etch and anodize wastewaters on dewatering characteristics of sludges in the aluminum finishing industry, data in Table 4 are presented. The data include specific resistance, filter yield and CST results for both segregated and conventional neutralization. The sludges generated by segregated neutralization could be concentrated by gravity sedimentation to a suspended solids concentration of 256.3 g/L whereas the sludge generated with the conventional technique could be concentrated to 36.1 g/L, only after much longer settling periods were used. Since filter yield and CST both varied with suspended solids concentration, in order to make a comparison between segregated and conventional neutralization, it was necessary to normalize filter yield and CST values to a fixed suspended solids concentration. Therefore, a suspended solids concentration of 35 g/L was arbitrarily selected for the comparison purposes.

As apparent from Table 4, specific resistance values at a pH of 7 and temperature of 80° C ranged from 2.3×10^{10} to 3.2×10^{10} m/kg and were about 10 times lower than those for conventional neutralization (i.e., 2.8×10^{11} to 3.8×10^{11} m/kg). Similarly, the filter yield value doubled to 9.6×10^{-3} kg/m^2·s from 5.71×10^{-3} kg/m^2·s and CST was halved to 25s

Table 3
Effect of Generation pH on Compressibility Constant

Generation pH	*Compressibility Constant*
5.5	0.48
7.0	0.44
10.0	0.34

from 53.7s with the application of segregated neutralization. More importantly, cake solids concentration, which is an indicator of manageability of a sludge for ultimate disposal, was increased to about 35% from 9%. In addition, with proper selection of neutralization pH (pH >7), cake solids concentration may be further increased and specific resistance may be reduced.

To further illustrate the impact of segregated treatment on sludge disposal problems encountered with conventional treatment, vacuum filter surface areas required to dewater each of the sludges in Table 4 are presented in Table 5. In addition, the total mass of wet sludge produced after dewatering is presented. The data were based on an assumed total mass flow of 938 kg/day of aluminum which was determined to be the mass flow of aluminum in spent etch and anodize wastewaters in an industrial plant.[10] It was assumed that, upon neutralization, all aluminum was precipitated as $Al(OH)_3$ and concentrated to 150 g/L by gravity sedimentation for segregated neutralization. The selection of the suspended solids concentration of the thickened sludge was based on the fact that all the sludges generated in this study were observed to settle to a concentration of 15% solids. Also, a 6-h shift of vacuum filter operation was assumed for sludge dewatering in these calculations.

The data presented in Table 5 clearly demonstrate that much lower filter areas and sludge volumes were obtained with the application of segregated treatment. At a pH of 7, a filter area of 3.14 m^2 is required for segregated neutralization as opposed to 22 m^2 required for sludges neutralized conventionally. Similarly, segregated treatment resulted in a sludge mass of 7,787 kg/d while conventional treatment produced 29,457 kg/d of sludge solids.

In summary, by the use of the segregated treatment technique, not only can significant reductions be achieved in the area of vacuum filters, but also a decrease in the sludge quantity and an improvement in sludge handling characteristics can be obtained.

CONCLUSIONS

The following conclusions can be drawn from this study:

1. Neutralization pH has a dramatic effect on the dewatering properties of sludges generated at 80°C using concentrated aluminum finishing wastewaters. Specific resistance and CST values of sludges decreased with increases in pH from 5.5 to 10. However, filter yield first increased in the pH range of 5.5 to 7.0 and then decreased with further increase in pH to 10. It was hypothesized that the decrease in filter yield at high pH levels was due to increased cake resistance which was not observed with the specific resistance test. Cake solids concentrations in filter leaf test experiments were higher at alkaline pH levels than at neutral or acidic pH levels.

2. No influence of feed suspended solids concentration on specific resistance was observed. However, CST and filter yield both increased exponentially with feed suspended solids concentration. Cake solids concentrations determined from the filter leaf test experiments were not affected by feed suspended solids concentration at pH levels of 5.5 to 7.0. However, they decreased with increases in the feed suspended solids concentration at pH levels of 8.5 to 10.

3. The relationship between specific resistance and vacuum pressure can be expressed by $r = r' P^{S_o}$ at any generation pH level. The compressability constant, s_o decreased with increasing pH levels and thus indicated the sludges were relatively incompressible.

4. Filter yield increased exponentially with an increase in form vacuum. The observation that the compressibility constant decreased with increasing pH levels was also supported by the relationship between filter yield and form vacuum. Cake solids concentration increased linearly with the increase in form vacuum.

5. Filter yield increased with the increase in time of cake formation. However, cake solids concentration was independent of time of cake formation at pH levels of 5.5 and 7.0 and decreased at when the pH was in the range of 8.5 to 10.

6. Dewatering properties of aluminum hydroxide sludges generated by segregated neutralization were significantly better than those of sludges generated by the conventional method at aluminum finishing plants. A decrease of 86% in vacuum filter area, and a significant decrease in the amount of wet sludge for disposal, were observed when the sludge generated at pH 7.0 and 80°C was compared with the sludge generated at pH 7.0 and room temperature with the use of conventional neutralization.

7. Aluminum finishing industries can substantially improve dewatering and handling characteristics of their sludges by the application of a segregated treatment system of spent concentrated etch and anodize wastes at high temperatures.

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Hazardous Waste Treatment Facility Siting Methods, Concerns and Progress?

Steven I. Taub[*]

ABSTRACT

The process of locating an area in which to construct a facility meeting all the relevant RCRA criteria for the treatment and disposition of potentially toxic and hazardous wastes is difficult, expensive, time consuming and extremely risky. This statement may evoke much controversy, but the inescapable conclusion that over the last several years it has been virtually impossible to implement the RCRA rules through the construction of new and needed processing facilities, is a fact that we must all, unfortunately, live with. At times it appears almost as if the RCRA rules, passed with all of the best possible intention, are nothing more than a roadblock to the development and use of new, innovative and much needed waste treatment technologies.

Stablex Corporation has firsthand experience in attempting to site plants utilizing such innovative techniques, and has indeed achieved a degree of recognition in that it has been granted a temporary interim delisting from the USEPA for 29 categories of potentially toxic and hazardous wastes. Stablex has even obtained permits for the construction of these facilities, but after more than four years of development and the expenditure of millions of dollars, still has not begun commercial operation. A plant permit sought in the Province of Quebec, Canada, however, has been granted, with construction underway as of October 1, 1981, after a process of only a little more than one year.

The reasons for the difficult siting environment shall be discussed from a firsthand viewpoint and specific proposals made to help augment the construction of the needed facilities.

CONCLUSION

In this paper I will introduce to you what we believe to be the origin of the problem of industrial toxic and hazardous waste disposition. I will explain something about Stablex Corporation, its development and its business. I will tell you about how we have gone about attempting to implement our business, which in effect was created as a result of the passage of the RCRA Act. I will review for you our long and arduous siting process in Groveland, Michigan which resulted in long litigation and is still unresolved even after four years of bitter debate and millions of dollars having been spent. I will cite the innovative approach that Stablex Corporation and the Gulf Coast Waste Disposal Authority took to place a regional treatment center into operation and the bitter opposition that emerged by not only well-meaning state citizens, but also by competitors who had a significant economic stake at risk. I will briefly discuss how reports that are written by well-meaning state officials can amplify certain facts and leave out others and be accepted as the total truth rather than as an edited version of the truth. I will discuss how the support of high-ranking state officials, for example the Governor of the State of Virginia, can lead to disappointment and no progress.

Stablex believes it can provide a part of the solution. We have never said that we are the entire solution, nor do we pretend that we will ever be. If Stablex had ten times the capital resources presently available to it it still could not provide all of the services needed to adequately treat and place the materials previously discussed. Therefore, we seek a start. We have made the offer that we will build a plant anywhere there is a reasonable market, at our own expense, to demonstrate that we can do exactly what we say. We make the offer again. We ask for assistance from community leaders and industrialists who recognize that now is the time to act to solve this most pressing of problems, the adequate disposition in an environmentally acceptable fashion of potentially toxic and hazardous wastes generated by industries serving all Americans and which industries allow us to enjoy the standard of living we currently have.

INTRODUCTION

The process of locating an area in which to construct a facility meeting all relevant RCRA criteria for the treatment and disposition of potentially toxic and hazardous wastes is difficult, expensive, time consuming and extremely risky. This statement may evoke much controversy, but the inescapable conclusion that over the last several years it has been virtually impossible to implement the RCRA rules through the construction of new and needed processing facilities, is a fact that we must all, unfortunately, live with. At times it appears almost as if the RCRA rules, passed with

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all of the best possible intentions, are nothing more than a roadblock to the development and use of new, innovative and much needed waste treatment technologies.

The RCRA Act was passed by Congress in 1976. The specific purpose of the law was to "provide technical and financial assistance for the development of management plans and facilities for the recovery of energy and other resources from discarded materials and for the safe disposal of discarded materials, and to regulate the management of hazardous waste." Clearly, a major intent of Congress was to ensure that all citizens of the United States of America be protected from potential adverse environmental impacts as a result of improperly managed and poorly handled waste disposition facilities. Congress further attempted by this landmark law to make practical by technological innovation new and environmentally compatible techniques to treat and detoxify and/or destroy the bulk of potentially toxic and hazardous wastes. Congress reasoned that if the old and environmentally unsound techniques and processes then in existence, many of which are still in existence, could be made either unlawful or economically uncompetitive or burdened with excessive potential liabilities, that users of such facilities would be forced to develop and/or utilize services employing more technologically advanced methods and techniques. It also recognized that government expenditures, which this administration is rightly dedicated to reduce, would continue to make large sums of finance available for clean-up operations. Many of these methods and techniques were available, although in pilot-type stages, in the early 1970's and Congress, with advice from EPA and other environmental groups, believed that the implementation and further development of these technologies could be accomplished in a timely fashion such that a major portion of the adverse environmental impact taking place at the time the law was passed could be curtailed and/or eliminated over the next decade.

Congress also recognized that the law needed public support to make it work. Congress believed that public support was present. This was implied through the limited protests received from the public and the overwhelming support of environmental groups, local and state politicians, regulatory authorities, and the EPA. Therefore, Congress believed that it was passing a popularly supported Act and that its implementation would be only a matter of time through the development of necessary needed rulemaking and enforcement procedures. What Congress did not take into account, however, was the developing concern among citizens and environmental groups with regard to the siting of new and technologically efficient facilities to replace environmentally inefficient existing facilities. Congress believed that the implementation of the rules would be a public mandate. What it did not recognize is that implementation of the RCRA rules and law would be subject to adverse citizen pressure brought about by a public misconception of what the RCRA rules really meant. Citizens had the clear feeling and conception that the development of facilities to handle potentially toxic and hazardous wastes would cause grave and considerable environmental problems. However, the citizens clearly were not, and still are not, willing to accept the fact that in the main the current disposition of toxic and hazardous waste is not being handled in an environmentally sound manner, and that this was a major purpose for the Act to begin with.

One is tempted to get philosophical about the solution to the problem. That is, the employment of new and modern technology to solve a problem perceived by Congress and the nation in the mid-1970's. The philosophy could go something like this: The nation, after experiencing a rapid and great industrial revolution and becoming the most efficient manufacturing country the world has ever known, provided enough goods and services to raise the standard of living to previously unknown levels and consequently the expectations of citizens ran somewhat ahead of reality. Much of the industrial development the country experienced between the early and mid-1900's occurred with minimal overall resource planning. Such a view became more prevalent in the late 1960's and still exists today. Most industries now evaluate a project on its full impact basis. That is, not only the economic merits of the process and technology with regard to the installation of the facility and the operation of the facility, but also the social ramifications resulting from such an operation. These results could be environmental results, community and social results, etc. Therefore, we have a national dilemma. Simply stated, the public perception that, "We can do anything we please to do, but not make any sacrifices whatsoever to do those things that we must do, wish to do and need to do", is in flux and it takes time to face up to new realities.

Helping to foster this viewpoint and creating an even more difficult environment in which to operate, we also have the pressures that motivate political leaders to either action or inaction. Politicians and those employed by them, i.e. bureaucrats, are prone to change viewpoint due to extreme public pressure that they perceive to cause them potential political harm, even though many of the individuals and groups raising these concerns represent a small minority of citizens.

Many citizens believe that since the RCRA Act was passed and states have been mandated to implement rules, the problem has disappeared and it is no longer of major concern. What the citizens do not understand is that the law was simply the first step of a process designed to eliminate current unacceptable practices which may lead to harmful results. The harm is not only from pollution of the land and groundwater, but also from the economic burden placed on industry and society when pollution events cost more to correct than the offending company can afford.

Stablex Corporation has been at the forefront in attempting to establish cost-efficient environmental control facilities designed to satisfy RCRA requirements and mitigate against potential environmental harm by the use of the newest and most modern technology available for the treatment of certain types of waste materials. The company has been engaged for several years in the development of its process and technology in the United States. The technology has been employed in England successfully for the last several years, and a major facility is planned for construction in Canada in the near future. In each location in which the company has attempted to begin operations, whether the locations be in England, Canada or the United States, severe and strong public opposition has been "part and parcel" of the development process. What is interesting and intriguing, however, is the fact that the establishment of facilities in countries such as England and Canada apparently are seen as beneficial to the overall community in an economic and environmental sense. The politicians and bureaucrats, although being subjected to substantial public pressure from relatively small groups of citizens, have listened to all citizen complaints. They have ensured the facilities would conform to all public concerns by adding permit amendments which reflect the public's concern for maximum safety with minimum risk. What has happened, however, is that in the United States the public officials have not yet recognized the importance of taking a firm stand to assist the development of facilities that are designed to answer the public need. They believe that time will change public attitude and, in turn, the needed facilities will be constructed sometime in the future. Until that occurs, however, the practices and procedures that have been of concern to citizens and government are still in force and in progress. Furthermore, it is a matter of concern as to whether or not the examples of Love Canal, etc. are just tips of an immense iceberg of malpractice below the surface. The question that should be posed in every community is do you wish to ignore the uncontrolled malpractices still prevalent today, only to wake up one day surrounded by another Love Canal or do you want to participate in a controlled, disciplined, modern technologically administered industry in which safe methods of handling the problems prevail?

The same environmental potential contamination which occurred in the 40's, 50's, 60's and early 70's which brought about the RCRA Act, still occurs because the implementation of new technology has not taken hold. The basic reason that the technology has not taken hold is not because companies have not wished to spend money to develop facilities, but because no community has been willing to accept a facility. Therefore, corporations in the business of converting or treating potentially toxic and hazardous wastes and removing their potential toxicity or mitigating it, and the generators creating the waste materials that must be treated, as well as the citizens demanding proper environmental treatment and disposition, and the federal and state governments which have the structures and the rules to implement and force such solutions, are all caught up in the problem of the inability to act. This inability is directly related to public pressure and concern.

It is Stablex Corporation's view that this public concern and misconception can be dramatically changed by the establishment of facilities to demonstrate that they can operate in an environmentally acceptable fashion and eliminate much of the potential hazard associated with the disposition of wastes generated by American industry today.

Stablex Corporation

After reviewing the Introduction, it is quite possible that it could appear that Stablex Corporation has been engaged in a sociological development rather than a technological development. I think we have indeed been engaged in both. Stablex Corporation is a company engaged in the business of converting potentially toxic and hazardous wastes that are essentially inorganic in nature to an environmentally inert final product. This product, STABLEX, is a material that has been tested by several independent laboratories not associated with Stablex Corporation. The results of these tests and other reviews have led the United States Environmental Protection Agency to classify STABLEX material on an interim basis as a non-hazardous material when produced from twenty-nine different categories of waste materials.

The process was developed in the late 1960's and brought to commercial fruition in the early 1970's in the United Kingdom. After several years of successful operation, the process was brought to North America. The process technology, called SEALOSAFE technology, takes several steps to accomplish. First, prior to accepting material for processing at a process plant, the material must be tested to determine if it can be successfully treated through the SEALOSAFE technology. It should be noted that the SEALOSAFE technology is geared toward, for the most part, large-scale regional treatment facilities which take a wide variety of potentially toxic and hazardous industrial waste materials and combine them so that their synergistic properties can be utilized to decrease the costs of conversion. Also, because of the large-scale nature of the facility, the capital employed per unit processed is decreased to the point that the process economics are more than competitive with existing techniques for the disposition of industrial hazardous wastes, namely dumping onto the ground or into the ground. Recently, however, it has come to the attention of Stablex Corporation that there are circumstances in which it may be economically feasible to establish a facility for a sole-source generator of waste materials. Usually this is accomplished for a rather large sole-source generator such that the economics are competitive with alternative techniques. One thing the generator must do when comparing competitive costs is to include the decrease in liability through SEALOSAFE as compared to controlled dumping. Dumping onto the ground, even with controlled double-liner systems, runs a relatively high degree of risk of adverse environmental impact when compared to the conversion or detoxification of waste materials.

Since the establishment of Superfund and other funds including certain state authorized programs, it has become increasingly more feasible economically to establish facilities that can travel from one location to another and process a relatively small amount of material at each stop. This "portable plant" approach is currently under consideration by a wide variety of industries for several uses. Basically, industry is examining this approach for the cleanup of old ponds and lagoons or the conversion of stored waste materials on a time-cycle basis such that the materials can be converted and placed on their premises to eliminate liabilities associated with comingling in a landfill environment.

After the material is tested for compatibility for the SEALOSAFE process and the successful conversion to STABLEX material has been accomplished, the client is given a quote for the service required. The quote can take several forms. If it is to be a portable plant type quotation, then personnel time on-site as well as processing costs and material costs, etc. are taken into account. Stablex Corporation does not license this technology and therefore requires that the plant be operated by Stablex personnel. There are, however, intermediate mechanisms to allow the establishment and operation of an on-site facility to make the facility fit into the operation policy of the host organization. Of course, if the material were to go to a regional treatment center, a price is given for the service, including trucking, etc.

For the regional treatment scheme, once the material enters the facility it must first be re-examined to determine if it has the same quality and character as that originally contracted for. This may also be done at an on-site type facility. Once the cross check is complete and the material is determined to be essentially the same, it is then accepted for processing. If the material is not determined to be the same as initially contracted for, and cannot be properly treated, it is rejected. If the material is suitable for conversion it is either sent back to the generator or a new price is negotiated. The material is then routed to a proper storage vessel for further treatment. Treatment may include several steps and the first step starts with the proper storage of the waste. Again, in a sole-source or on-site facility this process would be easier to accomplish because the amount of materials to be stored and pretreated would be known. If necessary, the material is pretreated to ensure that it can be put into a state necessary for ultimate conversion to STABLEX. Prior to the final step in the processing operation, waste materials which have been pretreated are combined with many other wastes and are then tested to ensure that the final material ultimately made from this mixture will meet specifications well within the EPA guidelines for a non-hazardous material. Once this is accomplished, the material is sent for final processing.

Final processing consists of the addition of cement and pozzolan to the pretreated slurry. The pretreated slurry, in combination with the cement and flyash, produces the final STABLEX material which has the characteristics of good structural integrity and environmental inertness. The placement of this material is a key to the success of the operation. Stablex practices different placement techniques, and insists that it be involved in the actual placement operations to ensure the satisfactory performance of the final material. Stablex Corporation believes it is in it's best interest and the client's best interest to maintain the placement area to ensure the material produced can achieve its ultimate integrity and, therefore, provide the benefits of environmental inertness and limited liability to the producer of the initial waste material. In less controlled situations, generators run the risk of subsequent site malfunction with lawsuits aimed at the financially strong generators who have used the site in the past.

Samples are taken of the product produced and subsequently tested. Records are kept for the authorities and for the generator.

Siting Case Histories

With regard to the siting of a plant to convert essentially inorganic, potentially toxic and hazardous waste material to the non-hazardous final material, STABLEX, it is time to turn our attention to cases where Stablex has experienced difficulties that can be expected to be encountered in siting such facilities. There are several facility studies that are important and relevant to discuss. **The ones that I shall address are Groveland Township; Oakland County, Michigan; Harris County, Texas; and** Hooksett, New Hampshire. I will briefly discuss Buckingham County, Virginia. Also briefly discussed will be Stablex Corporation's sister company's experience, Stablex Canada Limited, in siting a facility in the Province of Quebec.

• GROVELAND TOWNSHIP - OAKLAND COUNTY, MICHIGAN

In late 1977 a delegation led by the Governor of the State of Michigan visited the United Kingdom. This was during a period of time when the Stablex Corporation in the United States was being organized by the companies which developed the SEALOSAFE technology in the United Kingdom. After discussing the potential for the development of a facility which could convert potentially toxic and hazardous inorganic materials to STABLEX with the Governor of Michigan, Stablex Corporation shareholders, in the United Kingdom, decided that a fertile area for development in the United States would be the State of Michigan. A team was assigned for the purpose of developing a site and beginning the construction of the first SEALOSAFE technology facility to be operated as a regional treatment plant in the United States. Several contracts were made with the Michigan State Development Authorities and the Michigan Department of Natural Resources (DNR). In the early part of 1978 the Michigan Department of Natural Resources advised Stablex Corporation representatives concerning certain areas of the State of Michigan which were proposed for development by the State Economic Development Authority. After doing some preliminary engineering planning it became evident that only one of the sites had many of the ingredients necessary to establish a facility to process waste materials. The particular site located in Groveland Township, Oakland County, Michigan is adjacent to a modern interstate highway, approximately 35-40 miles north of the city of Detroit, and in a major inorganic hazardous waste generating area. The site also has a great need for restoration, in that approximately 150 of its 200 acres have been mined successively for over 40 years. The pits present at the site are as deep as 50 feet and the only realistic method available for land reclamation is the placement of an inexpensive fill-type material to bring the land up to grade.

The owners of the site had been in negotiations with the local community for several years due to their proposed development of a sanitary landfill at the site. The Town passed some restrictive zoning ordinances to bar the establishment of the sanitary landfill, although the State had already issued all necessary permits for its operation. After a lengthy series of discussions which lead to a court trial, a Consent Judgment was entered into by the Town and the sand and gravel pit owner. Effectively, the Consent Judgment ordered that the land be restored and brought to near grade using an essentially inorganic, non-combustible, non-flammable, environmentally inert material. The Town thought the language utilized in the Consent Judgment would clearly obviate the establishment of a sanitary landfill. Stablex Corporation, after negotiations with the land owner, signed an Option Agreement to purchase the land. Stablex Corporation then approached the Town after previous discussions with state authorities. The first meeting, which was between a few Town Elders and some interested citizens, was not conclusive. A second meeting was called at which time Stablex Corporation could more fully develop and explain its plan. Prior to the second meeting being called, the Town decided that it did not wish to have a facility located within its borders that would process potentially toxic and hazardous material. Although they did not fully understand the proposal, the mere hint of the term, waste, especially toxic and hazardous, resulted in the Town having no part of the proposal. Stablex Corporation met with local environmental groups, including the Audubon Society, and several Michigan groups organized for environmental protection, and explained its proposal and met with little resistance. As a matter of fact, there was some outright support, although low key. The state government accepted Stablex Corporation's Environmental Assessment Statement which they had required to begin the permitting process. Next Stablex held a small briefing at which it discussed with the press its plans for the Groveland site. The briefing included models, pictorial representations, photos, etc. of the proposed facility and other types of facilities that were already in operation. No representatives from the Town came to this briefing although they were informed of it.

The Township next organized a meeting to be held at a local high school at which Stablex Corporation could present its story to the public. Approximately 550 people attended this meeting held at a local high school. Again, a major presentation was launched by Stablex Corporation explaining in reasonable detail the approach and the potential benefits to the community. As expected, the meeting was tense although reasonably controlled. The obvious tone of the people present was wholly and totally against the Groveland facility for the treatment of potentially toxic and hazardous materials and the reclamation of the ground with a non-hazardous final product. After several hours of discussion and questions and answers, it became clear that the individuals present were, for the most part, against the establishment of the facility.

Stablex Corporation next proposed to the Town Planning Board the establishment of the facility and submitted a Siting Plan and a Mining/Restoration Plan. The two separate plans were required by town ordinance. Meanwhile, prior to Stablex submitting its plans, the Town passed ordinances effectively restricting the operation of a facility such as the one Stablex was proposing by establishing what they called a "special waste category". The special waste category was established for material which was produced from a variety of materials which were at any time classed as waste. Even if the material produced was non-toxic and non-hazardous, it could not be placed in Groveland Township. This ordinance clearly meant to stop the establishment of the facility that Stablex proposed.

Stablex was rejected by the local Planning Board in its request for the establishment of the facility. Stablex had a dilemma. Should it leave the community and attempt to establish a facility elsewhere or should it seek a remedy by asking the Court to enjoin the Township from interfering with its lawful rights to establish a facility which was in accordance with all the pertinent rules and regulations as they existed in the town at the time they were initially applied for. Stablex's thinking was that it was necessary to seek relief against the Town because if it did not, then any other town wishing to stop the establishment of a Stablex-type facility could merely do the same thing, i.e. simply say they didn't want it, and then Stablex would find itself in the same position every place it went, effectively eliminating its business potential.

A motion was filed in the local Circuit Court in April, 1979 and lasted until April, 1980. By the time the Court reached its verdict, April, 1980, Stablex Corporation had spent over a million dollars developing the Groveland site, especially with regard to permit applications, court proceedings, etc., and was well on its way in the permitting process. The local Circuit Court found in Stablex's favor and issued an order enjoining the Township from interfering with Stablex in establishing a facility, and which stated that STABLEX material produced from such a facility is a non-waste material, a material that could be used for reclamation. Between April and November, 1980, Stablex Corporation had to go to court to force the State of Michigan to issue permits to it. The State of Michigan has decided that all the permit applications that Stablex had submitted to it were complete, but were stalling on the issuance of permits, primarily in Stablex's opinion, for political and other reasons especially associated with citizen pressure. Again the Circuit Court found in Stablex's favor and ordered the DNR to issue permits to Stablex, allowing it to begin the construction of its facility. These permits were issued prior to November 18, 1980 which effectively grandfathered the Stablex facility as an existing facility under the RCRA rules.

It should be noted that this exclusion from the RCRA rule process does not imply that Stablex Corporation is exempted from constructing the facility in accordance with RCRA. As a matter of fact, Stablex was issued an Act 64 permit by the State of Michigan. The permit was issued under a law passed requiring that Act 64 rules were to be modeled after the RCRA statutes. The unique part of the permits issued to Stablex by Michigan DNR was that the State recognized the waste treatment and reclamation center could be permitted with two separate permits. First a permit to treat and convert potentially toxic and hazardous waste material to a non-hazardous material, STABLEX, and second, a placement area which could accept the non-hazardous STABLEX material as a result of the technology employed in the processing facility. To the best of my knowledge this is the first time a state has taken this stand.

Stablex Corporation was now armed with two permits. One, a permit to construct a toxic and hazardous waste treatment facility to convert inorganic materials to STABLEX material; and second, a placement area which could accommodate the STABLEX material produced from this facility and in turn reclaim the land in accordance with the Consent Judgment the Town and land owners had agreed upon.

The EPA next received a request from Stablex Corporation to delist STABLEX material and the State of Michigan requested EPA for rapid action to classify STABLEX as non-hazardous material. EPA issued a temporary delisting in November, 1980 which meant that STABLEX produced from twenty-nine different categories of listed toxic and hazardous waste is considered non-hazardous. This corroborated the State of Michigan's stand with regard to the issuance of permits for land reclamation purposes.

Next, the Town appealed the Circuit Court decision and asked the Appellate Court to enjoin Stablex from continuing any construction during the appeal period. The Appellate Court granted the Township's request for injunction and Stablex was barred from continuing construction in December of 1980.

For Stablex to continue construction, the Appellate Court had to act. Stablex was at a standstill. Stablex asked the Township if it would consider negotiating to reach a mutually acceptable and agreeable solution. They refused. In May 1981 the Appellate Court found in favor of the Township and overturned the Circuit Court decision saying that if certain evidence had been introduced in the lower court, its verdict would have been different. This, in Stablex's opinion, is clearly against the admissible evidence rules as Stablex understands them and to clarify the issue, Stablex has lodged an appeal with the Michigan Supreme Court. To date, Stablex has spent or committed to the Michigan Project development about $4 million. There is no modern treatment facility in the State of Michigan. There is no placement area which places exclusively detoxified material in Michigan. All material placed in Michigan is placed in either a sanitary landfill or secure landfill. Many wastes are trucked out of the State of Michigan at great expense to Michigan industry. All the people employed in the Groveland area owe their livelihoods to Michigan industry. The Stablex facility to be located in Groveland, Michigan would be an employer of people and provide a reasonably high tax base because of the substantial capital investment Stablex had committed itself to, $20 million. So to date, four years after the start of discussions with regard to the establishment of a facility meeting RCRA standards in the State of Michigan, no facility has been constructed, but there is a facility with permits that can't be constructed.

Stablex has every intention to see its case through the Michigan Supreme Court and believes the outcome will affirm its arguments so that it can get on with helping to solve one of the most enormous problems confronted by the State of Michigan, the safe treatment of toxic and hazardous wastes.

- **HARRIS COUNTY, TEXAS**

In 1979 Stablex Corporation proposed to the Gulf Coast Waste Disposal Authority, GCWDA, that the Authority consider entering into an agreement with Stablex to allow Stablex to operate a toxic and hazardous waste treatment facility at a Gulf Coast-owned site. After due consideration, the GCWDA felt it would be in the best interests of the citizens of the tri-county area in which it has semi-governmental authority, to establish a regional treatment facility which could treat and detoxify a wide variety of waste materials, some of which may be inorganic in nature. The Authority went on a world-wide search for technologies to incorporate into this facility and studied many different and varying treatment methods either in use or proposed. After their exhaustive study, and several visits to facilities that were operating in various parts of the world, GCWDA chose Stablex Corporation to establish a facility for the conversion of potentially toxic and hazardous inorganic materials to the non-hazardous STABLEX material. They also chose another processor for incineration, and plan to choose other companies to deal with oil/water separation, solvent recovery, etc. Stablex Corporation, GCWDA, and the incinerator processor collaborated to submit permit documents to the State of Texas. The permit documents were submitted in mid-1980 and the relevant Texas authorities agreed the documents were in conformance with necessary standards for issuance. However, part of Texas law includes the holding of a series of several meetings at which the public can express their views, either technological or sociological. GCWDA, believing that it had political integrity on its side, felt the hearings would not be a major roadblock to the establishment of the regional treatment facility which was to be located at a site next to the Ellington Air Force Base, in an area previously used for a sand and gravel mining operation. No residences were close by and the land was used for reasonably low valued uses. A groundswell of opposition quickly developed. Among the opposition leaders were competitors who were concerned with the competitive nature of the facility proposed by the Gulf Coast Waste Disposal Authority. One of the competitors actually went to such lengths as to hire an individual to travel from place to place in Texas and throughout the United States, following Stablex Corporation developments and complaining about Stablex Corporation. This individual went as far as to submit to the U.S. Environmental Protection Agency a series of newspaper clippings as evidence of why Stablex Corporation should not be granted a temporary delisting for its material. The newspaper quotations and clippings, although containing not a shred of technical data or evidence, have of course been accepted by EPA in their evaluation only because of their sincere desire to ensure that all Americans have the opportunity to comment on environmental matters. This particular approach, although noble and worthy, needs in our opinion to be re-examined in some detail. The question arises as to what difference it makes if a newspaper in some part of the county believes that a facility may or may not do something good. That's an opinion and perfectly acceptable and reasonable in today's environment and society, but opinions are not necessarily fact and in our opinion fact controls the issuance of permits. Technological success in a social framework is the ultimate goal.

Because of the major uproar caused by the announcement of the planned facility adjacent to Ellington Air Force Base, the two companies and Gulf Coast Waste Disposal Authority re-examined their proposal for the establishment of the Ellington facility. On re-examination it was felt that perhaps the proposed facility should be moved to a more industrialized area. After spending something on the order of $1 million in the initial site development, it was decided to abandon the Ellington site and move to a new site in a more industrial area, the Bay Port site. The site selected was announced in October 1981. Although no organized opposition was expected, severe opposition is forming and is currently mounting. I can't report to you at the present time the actual outcome of this particular development, but I can only say it appears to be a repeat of the Ellington situation. The unfortunate thing involved here is that the State of Texas was actually involved, although peripherally, through a State of Texas organized corporation - Gulf Coast Waste Disposal Authority - in the site selection process and the permitting process. The state of Texas has so far been barred from the establishment of a facility that is so much needed in this area.

- **HOOKSETT, NEW HAMPSHIRE**

In late 1979 Stablex Corporation began to study the New England area as one that was in need of a facility to treat and process inorganic materials to STABLEX. After a careful selection process, Stablex came to believe that the best location for the establishment of a regional treatment facility was the State of New Hampshire. Visits were made to the State Office of Solid Waste. The State Office of Solid Waste was quite helpful and receptive to Stablex Corporation's visits and inquiries. Stablex also visited the State Economic Development Authority and discussed with them the development of a site to treat and process waste materials. Presentations were made to the State Senate Committee responsible for solid and hazardous wastes, as well as to several business and industry groups. After many discussions and considerations, a site in a town located outside Manchester, New Hampshire, in Hooksett, was chosen. The Town Selectmen were visited and informed of Stablex's selection. The Selectmen were in reasonable agreement that the Stablex proposal was realistic, reasonable and doable in Hooksett. A meeting was held at the local high school where Stablex presented its story and answered several questions of concerned citizens. No apparent opposition was noted at that meeting. As time went on, however, opposition began to mount, and by the time Stablex Corporation was in the process of preparing its submissions for Planning Board approval, substantial opposition existed. Stablex Corporation participated in several studies and trips organized by the people in the State of New Hampshire. First, a group of citizens from the Town of Hooksett visited the facility at the expense of the New England Regional Commission, which is a public entity located in Boston, Massachusetts. The citizens came back reasonably impressed, feeling that the Stablex facility could indeed do what Stablex claimed. That is, convert toxic and hazardous waste materials to a non-hazardous final product. Along with the citizens were representatives from the University of New Hampshire who wrote a report which said that "Based on an extensive analysis of existing data concerning the STABLEX process for solidification of hazardous waste and discussions with experts in the hazardous waste disposal field, it is our feeling that the Stablex proposal for Hooksett, New Hampshire will likely result in little impact on the environment." . . . "In summary we feel that all existing data at our disposal indicate that STABLEX is an environmentally safe material, that it will not pollute the groundwater, and that the Hooksett site is amenable to this process." Additionally, the newspapers were reasonably supportive to the establishment of the facility in Hooksett, and it was Stablex's opinion that the facility would be approved by the Planning Board. However, a visit was made by three officials from the State of New Hampshire to facilities utilizing SEALOSAFE technology in England. Prior to that visit Stablex carefully explained to these visiting officials that of the facilities that they were to visit, one facility was treating and processing inorganic materials and producing STABLEX material. The other facility had at one time done this, but since that time it had changed operation and was processing both organic and inorganic material, and is not producing STABLEX product. The officials insisted on visiting both facilities and Stablex concurred, because if Stablex did not it would have been accused of hiding something.

Along with the New Hampshire State authorities was a visitor from the State of Louisiana hired by the State of Louisiana to go and visit Stablex's facilities for evaluation purposes. First the individuals visited a facility located outside of Thurrock, England which processes only inorganic material. The State of New Hampshire visitors, although informed prior to their trip that it would be extremely difficult to take samples back to the United States because of having to deal with another company's management, insisted that samples be taken and as a matter of fact, took samples without permission from anyone. When it was noted to them that they had taken an unauthorized sample, they refused to give it back. This, of course, caused great consternation and rather than letting this develop into an argument, Stablex officials felt it was best to allow the New Hampshire officials to take their sample because Stablex Corporation officials knew and understood that the sample was perfectly safe and acceptable under the U.S. EPA rules. However, just to make sure the data developed by New Hampshire could be corroborated, the Stablex officials asked that half the sample be given to them for testing at the Thurrock laboratories that day. The testing was done in front of the New Hampshire officials. The data showed that the material passed the EPA requirements as a non-hazardous material.

The New Hampshire officials also visited the other facility that I mentioned earlier which processes both organic and inorganic wastes. On their return to the United States a report was written which was damaging to Stablex Corporation in that the visitors, for example, reported that leaking drums, old bags, and puddles were observed. Now anyone who has visited any processing plant, especially a plant that processes toxic and hazardous wastes, will know that wastes are sometimes not shipped in the newest type containers. Because a drum is leaking does not mean it will contaminate anything. The facilities are equipped with bermed areas to insure that leaks and spills are contained and routed to processing areas. The old bags may have been bags of material that were rejects from a production process and sent to the waste management facility for incorporation as a treatment chemical. The puddles could have been caused by leaks from drums, etc., which were contained behind bermed storage areas. The New Hampshire officials, however, avoided reporting that they took a sample and that the sample was tested and proved to be satisfactory. It was clear to Stablex Corporation officials that the individuals visiting from the State of New Hampshire were not interested in the truth, but were interested in creating a case to show that the SEALOSAFE process and its operation in England were questionable. It should be noted that the Louisiana consultant wrote a positive report which was dramatically opposite to the New Hampshire authorities' report. In Stablex's opinion, much of the reason the Township Planning Board ultimately rejected Stablex's proposal for the construction of a facility in Hooksett was due to the State of New Hampshire officials' report. Additionally, the Town of Hooksett followed in the footsteps of Groveland Township in that they passed an ordinance seeking to bar the disposition of toxic and hazardous wastes of any type in the Town of Hooksett unless those wastes were generated within the boundaries of the Town of Hooksett. Stablex Corporation, after being rejected by the Planning Board, challenged the ordinance and the rejection of the Planning Board in New Hampshire Superior Court. At present, the Court is determining the issuance of whether or not the ordinance passed was valid. It should be noted, however, that the State did file a Friend of the Court Brief in favor of the Stablex position that the ordinance passed by the Town was invalid. The State argued that if the Town of Hooksett were successful in utilizing this type of procedure to regulate the processing and treatment of potentially toxic and hazardous wastes, there would be nothing to stop every other town in New Hampshire from doing the same and therefore, the entire framework of the State rules and regulations concerning the disposition of toxic and hazardous wastes would be moot.

Stablex believes it will prevail in court with regard to the issue of the ordinance. Stablex wishes to construct and operate a facility in Hooksett at the earliest possible time. To this end, Stablex filed a set of permit applications in September of 1980. The permit applications were first reviewed by the New Hampshire authorities in June of 1981. Immediately after the New Hampshire authority review, Stablex was informed that the permit applications which had been sitting on their desks for nearly eight months were incomplete and further information was requested. Stablex provided such information in November of 1981 and is currently waiting to hear from the State of New Hampshire if the applications can now be considered complete. In the meantime, New Hampshire industry has no outlet in the State of New Hampshire for the potentially toxic and hazardous wastes that it generates. Wastes must travel in some cases hundreds of miles for ultimate disposition. This is extremely costly for the industry of the State of New Hampshire, but to our surprise no industry in New Hampshire has raised its voice in protest over the actions the State has deemed necessary to impose on Stablex.

Stablex continues to pursue its objective in New Hampshire. That is, the establishment of a plant to treat and convert potentially toxic and hazardous waste to STABLEX material, and the corporation is planning to construct such a facility as soon as reasonably possible.

- **BUCKINGHAM COUNTY, VIRGINIA**

The case of the establishment of a facility in the County of Buckingham, Virginia is most interesting. Stablex discovered in May of 1981 that a permitted facility existed in Buckingham County, Virginia which was authorized by the EPA and the State of Virginia to accept various types of potentially toxic and hazardous wastes for disposal. The disposal practiced was, and still is, land placement in clay-type soil with the standard coverage procedures. The material being accepted at this site consisted mainly of furniture industry wastes, mainly organic in nature. Stablex Corporation believed that the permits that the site operator had could be modified such that a Stablex-type facility could be constructed and operated. Stablex believed that its approach to the Buckingham Site would be extremely beneficial to the residents of Buckingham County and to the State of Virginia. The reasoning went something like this - The site is currently being used for ordinary dumping. Stablex brings a high-technology processing facility to the site to convert various types of toxic and hazardous wastes to a non-hazardous material, thereby decreasing the likelihood of any adverse environmental impact resulting from the use of the site. Additionally, the State of Virginia benefits because a facility offering services to treat inorganic materials would be present.

The problem Stablex foresaw, however, was the site had been used for a number of years for the placement of this furniture industry type waste in addition to ordinary garbage and refuse. A potential liability existed, on Stablex taking over the site. Stablex felt that it would be in their best interest as well as the State's best interest to attempt to mitigate against this potential liability prior to proceeding. Stablex approached the State and suggested that the State purchase the site and Stablex then lease from the State on a long-term basis, thereby having the State then accept the liability for the older sanitary landfill/furniture waste placement area. The State discussed this approach with Stablex Corporation several times and believed that it was feasible and reasonable. Stablex Corporation discussed its approach with the Governor of the State of Virginia, who put his support directly behind the project.

All that was left to do was to have the State Board of Health approve the arrangement to enter into a tri-party agreement between Stablex, the site owner and the State for the State to purchase the land and Stablex to lease it on a long-term basis.

The State next went to the County and discussed with the County the plan to acquire the site and to allow Stablex to construct its facility and operate there. The local officials were immediately concerned and alarmed. It's uncertain whether their concern and alarm was due to the fact that they were not fully informed from the very beginning about the project, or that the project was about to be undertaken without their advice and consent. At any rate, the officials sought an injunction to stop the State from acquiring the site. The local judge granted the injunction. The injunction was challenged in the Virginia State Supreme Court by the State Health Board to proceed with its plan to acquire the site and have Stablex begin its site studies and specific permitting for it, followed by plant construction. During this time a groundswell of public opposition developed. Everyone apparently missed the point that the site had already been used for several years as a toxic and hazardous dump. The process proposed for the site was an upgrade to the site with substantial capital investment being committed to it. This however was of no importance to the opponents of the site. The opponents eventually forced the State Health Board to enter into a study to determine which sites in the State of Virginia could be utilized for the development of a toxic and hazardous waste placement area in the State of Virginia. The study is planned to take at least six months.

When this happened, the Buckingham County officials approached the site owner and offered to buy the land from him for their own use, thereby circumventing any potential use by Stablex or the State for the establishment of a SEALOSAFE-type facility. The situation as it presently stands is in flux and it is difficult to report on the ultimate outcome of this development. All that can be said, however, is that this was a development that had the support of a Governor and of a Health Board. Such support withered in the face of the enormous public pressures placed upon these officials by the citizens of Buckingham County, a small Virginia county. The difficult point for Stablex to understand is that the site is already utilized and has been for several years as a dump. Stablex wished to upgrade its use, thereby minimizing the problems that could be generated as a result of the continued operation of this type dump. That has not occurred as yet.

What Can We Learn?

With the case histories cited in the previous section as a basis for at least an understanding of the experience that Stablex Corporation has been through in attempting to permit a RCRA type facility to answer the crying need to develop proper and economically competitive control facilities, it may be possible to extract some kernels of knowledge.

In my opinion it appears that technology really is not the determining factor in siting a facility. True, technology is the motivating force behind a company such as Stablex in attempting to develop its business, which offers an environmentally acceptable solution to ordinary dumping. However, the more fundamental hurdle is to convince local populations as well as their political leaders and the bureaucrats who work for them that the installation of such facilities will in the end be in the public's best interest. The exact methodology to convince people to accept a good and worthy solution to a continuing problem is extremely complex.

Stablex is a company wishing to spend its own capital resources to develop an industry to serve other industries and, in turn, people. It is caught up in the mid-1900's syndrome. That is, growth at any price is unacceptable, and therefore any new facility that may be productive in nature is looked on with great suspicion. If one can examine the development of recent projects within the United States, it's reasonably clear that many of them have been substantially curtailed or in come cases stopped completely by overwhelming public opposition, even at the cost of jobs and economic viability to the communities which opposed them. People are convinced that the "pursuit of the good life" could be severely hampered by the development of what they perceive to be unwelcome neighbors in the form of industrial corporations which add to the overall wealth of the community and society. Stablex Corporation is caught up in the same maelstrom of debate and philosophy. It goes unrecognized, however, that hand-in-hand with the pursuit of the good life are the services necessary to ensure it can continue. Services as essential as garbage collection, water supply, sewage, food, electricity and heat must continue. Many of these activities are productive, profit-making enterprises and accepted as necessities by society. Some of them may be considered repugnant in nature, but it still is necessary and important to continue the supply of their services. Society considers the dumping of garbage and refuse a repugnant but necessary service. Towns usually allow the operation of refuse disposal areas only after they have been forced into this solution and no alternatives exist. Additionally, the older placement areas utilized for the disposal of toxic and hazardous wastes are usually located in an outlying area or in a depressed area where the local populous is either not present or not as vocal as those in more affluent areas. Stablex Corporation, although providing a service much more technologically advanced than dumping, is cast in the same role as the garbage dump. Because of this, and because there is no real need in many communities to specifically have a toxic and hazardous waste treatment and resultant non-hazardous material placement area located within the borders of the town, the town fathers usually take the more expedient way out and side with the small but extremely vocal minority that for the most part is committed to clearly resist any change.

One is tempted to consider the cessation of activities leading to the development and commercial operation on new technologies and their implementation for waste disposition. The result of this would be continued dumping practices which society has recognized as unacceptable, but has not yet accepted their responsibility of dealing with it.

It is Stablex's view that the most essential point in the location and subsequent development of a facility to treat toxic and hazardous wastes and to change their character to a more environmentally acceptable form, is the support of committed local citizens and their political leaders to ensure that overriding community needs can be answered. This takes courage. It takes conviction and it takes the understanding and belief that unless the problem is solved somewhere in a satisfactory manner, it will continue to be swept under the rug in an unacceptable fashion. Stablex seeks to work with the community leaders to help them understand the nature of its process technology and what it wishes and plans to do. Stablex stands ready to assist the community and provide benefits to them as a result of their allowing these facilities to be constructed.

We are at a critical juncture. Siting facilities is the fundamental issue. To date, we are unaware of any proven means to develop and locate a facility. Stablex certainly has no wish to continue its development through court suits. It believes in the end it will prevail, but look at the total cost in continued improper dumping of wastes.

PROPOSED SOLUTIONS

The only solution I can offer is a plea for you to think through in a thorough, logical, and concise manner the problem as it currently exists, their need for a solution, and the proposed solution. Many of you who have read this paper will decide that the problem is not really your problem. Others will feel that their particular toxic and hazardous waste problems are being adequately taken care of. Still others will decide that someone else will take care of the problem and the issue. I am interested in talking to those few of you who have a commitment to institute modern methods designed to minimize liability and environmental harm.

The solution really lies with you the reader. It lies with your communities in recognizing the need and being courageous enough to accept the challenge of providing a solution. It lies with your industry, in understanding its liability exposures and its potential for contingent liabilities and its willingness to become good citizens in their communities. In addition, it lies with industry in recognizing that the problem is not solved by shipping wastes 100 or 1,000 miles away and not really understanding their ultimate disposition.

CONCLUSION

In this paper I have introduced to you what we believe to be the origin of the problem of industrial toxic and hazardous waste disposition. I have explained something about Stablex Corporation, its development and its business. I have told you about how we have gone about attempting to implement our business, which in effect was created as a result of the passage of the RCRA Act. I have reviewed for you our long and arduous siting process in Groveland, Michigan which resulted in long litigation and is still unresolved even after four years of bitter debate and millions of dollars having been spent. I have cited the innovative approach that Stablex Corporation and the Gulf Coast Waste Disposal Authority took to place a regional treatment center into operation and the bitter opposition that emerged by not only well-meaning citizens, but also by competitors who had a significant economic stake at risk. I have briefly discussed how reports that are written by well-meaning state officials can amplify certain facts and leave out others and be accepted as the total truth rather than as an edited version of the truth. I have discussed how the support of high-ranking state officials, for example the Governor of the State of Virginia, can lead to disappointment and no progress.

Stablex believes it can provide a part of the solution. We have never said that we are the entire solution, nor do we pretend that we will ever be. If Stablex had ten times the capital resources presently available to it, it still could not provide all of the services needed to adequately treat and place the materials previously discussed. Therefore, we seek a start. We have made the offer that we will build a plant anywhere there is a reasonable market, at our own expense, to demonstrate that we can do exactly what we say. We make the offer again. We ask for assistance from community leaders and industrialists who recognize that now is the time to act to solve this most pressing of problems, the adequate disposition in an environmentally acceptable fashion of potentially toxic and hazardous wastes generated by industries serving all Americans and which industries allow us to enjoy the standard of living we currently have.

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Disposal: What Does It Really Cost?

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ABSTRACT

In past EPA and AES Seminars the electroplaters have heard a number of papers dealing with in-plant modifications, conservation of water and chemicals, ways to minimize sludge and how to recover water and chemicals by a variety of methods. Despite all the information presented over the years very little has been done in the majority of plants to implement the recommendations provided by these papers. While some of the recovery technology is quite expensive and might be rejected on budgetary grounds, this argument does not prevail for many of the inexpensive recommendations. It appears that indifference or lack of motivation on the part of many platers has inhibited a serious attack upon waste in the plating room. These same people voice complaints about the high capital costs of wastewater treatment equipment.

Waste is still the crux of the matter. Water and chemical waste impacts not only upon the size and cost of the treatment equipment, but also upon manufacturing costs and waste treatment costs. Some say that inactivity or indifference indicate a lack of motivation. This paper presents motivational material in the form of dollars and cents figures for plating bath make-up costs, together with chemical treatment costs, sludge generation rates, and disposal costs.

The motivation needed to persuade the metal finishers to conserve and/or recover chemical values must reside in the realization of the real costs of waste. The initial cost of a chemical bath is only a fraction of the costs associated with chemical waste. The term "chemical" is used here because as will be seen, it is not just metals that are involved in the cost of wastewater treatment. Admittedly, electroplating baths represent a significant cost to the metal finisher, and it is these make-up costs that will be examined first.

The bath make-up cost for a representative chromium plating bath is shown on a dollar per gallon basis in Table 1. The formulations presented in this paper are largely of the handbook variety and the costs presented are generic prices as prevailing in November 1981. It might be said that make-up costs would be higher had proprietary prices been used. The reader would be advised to compare the composition and costs presented here with those actually experienced in his plant.

Most readers are well aware that the hexavalent chromium employed in chromium plating requires reduction to the trivalent state prior to precipitation. Table 2 summarizes some of the most commonly used chemical reduction methods, and shows some of the treatment costs associated with the various methods.

There are some surprising differences in treatment costs, which may cause some to reconsider previous attitudes. Keep in mind at this point that we have not yet reached "the bottom line," and that there are more cost factors to be added.

Note that the treatment costs refer to a nominal dragout rate of one gallon of plating bath per hour. In order to obtain real treatment costs, the reader need only multiply (or divide as the case may be) by the actual measured dragout rates prevailing in his operation. A number of papers and articles have described ways to measure dragout rates, but essentially all rely upon measurement of metal concentration in a fresh water rinse tank after one or more racks or barrels have been processed. If the reader really wants to know how much waste is costing, he would be well advised to determine dragout rates for *all* process tanks. Motivation for this activity will be developed as this presentation progresses. Many will say they can't be bothered with all that fooling around and the expense of doing all those chemical analyses: but the effort and expense may well be returned by motivating changes in wasteful practices.

Just as hexavalent chromium requires pretreatment, most readers are also well aware that cyanides require oxidation prior to precipitation of the metal content. In order to establish base costs, Tables 3, 4, 5, 6 and 7 present make-up cost figures for common cyanide baths on the same one gallon basis as presented previously. The silver and gold baths are so expensive that no one should need encouragement to recover these values, yet some stupidity is still prevailing with waste of these metals. The cost of treating silver and gold solutions will not be considered here, in the hope that after seeing these make-up costs, silver and gold will not appear in plant effluents.

The oxidation of cyanides is usually accomplished by alkaline chlorination using either chlorine or sodium hypochlorite. The chemistry of the reactions involved are summarized in Figure 1. Notice that the oxidation of cyanide to carbon dioxide (carbonate) and nitrogen proceeds in two stages. The first stage, conversion of cyanide to the intermediate cyanate, is usually acceptable treatment for small (under 10,000 gallons per day) dischargers to POTW sewers. Larger dischargers and stream dischargers are usually required to apply the two stage oxidation, and

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Table 1
Chrome Bath
Make Up

Formula	Conc. (oz/gal)	Cost/Gal
CrO_3	25	$2.34
H_2SO_4	0.25	$0.01
	Total Cost/Gallon	$2.35

Table 2
Treatment Costs
1 Gallon Chrome Plating Bath

Treatment Chemical	AMT (lbs)	Cost	Total Cost
Ferrous Sulfate + Sulfuric Acid	6.76+2.38	$1.49+$0.11	$1.60
Iron + Sulfuric Acid	0.45+2.38	0.05+0.11	0.16
Sodium Bisulphite + Sulfuric Acid	1.26+0.60	0.55+0.03	0.58
Sulphur Dioxide	0.78	0.17	0.17

Table 3
Zinc Bath-Cyanide
Make Up

Formula	Conc. (oz/gal)	Cost/Gal
$Zn(CN)_2$	4	$0.48
NaCN	2	$0.09
Na_2CO_3	14	$0.21
NaOH	13	$0.24
	Total Cost/Gallon	$1.02

Figure 1
Cyanide Oxidation Equations

1. $NaCN + 2NaOH + Cl_2 \rightarrow NaCNO + NaCl + H_2O$
2. $2NaCNO + 4NaOH + 4Cl_2 \rightarrow 2CO_2\uparrow + N_2\uparrow + 8NaCl + 3H_2O$
3. $2NaCN + 10NaOH + 5Cl_2 \rightarrow 2NaHCO_3 + N_2\uparrow + 10NaCl + 4H_2O$
4. $2NaCN + 5NaOCl + 2NaOH \rightarrow 2Na_2CO_3 + N_2\uparrow + 5NaCl + H_2O$

Table 4
Cyanide Copper Bath-Make Up

Formula	Conc. (oz/gal)	Cost/Gal
CuCN	3.5	$0.61
NaCN	4.6	0.19
Na_2CO_3	4.0	0.06
NaOH	0.5	0.01
Rochelle Salt	6.0	0.62
	Total Cost/Gallon	$1.49

Table 5
Cadmium Bath
Make Up

Formula	Conc. (oz/gal)	Cost/Gal
CdO	3	$0.55
NaCN	10.4	$0.43
Na_2CO_3	6.0	$0.09
NaOH	1.9	$0.04
	Total Cost/Gallon	$1.11

Table 6
Silver Bath
Make Up

Formula	Conc. (oz/gal)	Cost/Gal
AgCN	4.8	$47.18
KCN	8.0	$ 0.69
K_2CO_3	2.0	$ 0.06
	Total Cost/Gallon	$47.93

Table 7
24 Karat Gold
Bath-Make Up

Average Concentration Au	1 oz/gal
Average Price Au	$450.00/oz
Cost/Gallon	$450.00

economic impact of this additional treatment is particularly obvious. Treatment costs for one gallon of plating bath with both single and two stage oxidation are tabulated using both chlorine gas and sodium hypochlorite in Tables 8, 9 and 10. Table 11 summarizes the costs shown in these tables. The reader can, as with previous tables, compute actual treatment costs for his specific situation.

In order to compare cyanide versus non-cyanide plating baths, with regard to first costs and treatment costs, Tables 12 and 13 present non-cyanide bath make-up costs on a gallon basis for zinc and copper. While these formulations may not agree with reader's preferences, they provide a working basis for the treatment and disposal costs to be presented. Table 14 presents make-up costs for a nickel bath to round out a fairly representative selection of metals and baths. The theoretical quantities and costs for both lime and sodium hydroxide required to precipitate each of the metals given in the formulations at the rate of one gallon per hour for eight hours is given in Table 15. Note that these figures are theoretical and in actuality more alkalinity is required. If

Table 8
Treatment Cost
1 Gallon Zinc Cyanide Plating Bath

Treatment Chemical	1st Stage CN TMT AMT (lbs)	1st Stage CN TMT Cost	1st & 2nd Stage CN TMT AMT (lbs)	1st & 2nd Stage CN TMT Cost
Sulfuric Acid				
2nd stage CN tmt		—	0.01	$0.01
Sodium Hydroxide				
1st stage CN tmt using Cl_2	0.56	$0.08	—	—
1st & 2nd stage CN tmt using Cl_2	—	—	1.39	0.21
1st & 2nd stage CN tmt using NaOCl	—	—	0.15	0.02
Chlorine				
1st stage CN tmt	0.50	0.13	—	—
1st & 2nd stage CN tmt	—	—	1.22	0.32
Sodium Hypochlorite				
1st stage CN tmt	0.51	0.31	—	—
1st & 2nd stage CN tmt	—	—	1.29	0.77

Table 9
Treatment Cost
1 Gallon Cyanide Copper Plating Bath

Treatment Chemical	1st Stage CN TMT AMT (lbs)	1st Stage CN TMT Cost	1st & 2nd Stage CN TMT AMT (lbs)	1st & 2nd Stage CN TMT Cost
Sulfuric Acid				
2nd stage CN tmt	—	—	<0.01	$0.01
Sodium Hydroxide				
1st stage CN tmt using Cl_2	0.65	$0.10	—	—
1st & 2nd stage CN tmt using Cl_2	—	—	1.62	0.24
1st & 2nd stage CN tmt using NaOCl	—	—	0.17	0.03
Chlorine				
1st stage CN tmt	0.58	0.15	—	—
1st & 2nd stage CN tmt	—	—	1.43	0.38
Sodium Hypochlorite				
1st stage CN tmt	0.60	0.36	—	—
1st & 2nd stage CN tmt	—	—	1.50	0.90

Table 10
Treatment Cost
1 Gallon Cadmium Plating Bath

Treatment Chemical	1st Stage CN TMT AMT (lbs)	1st Stage CN TMT Cost	1st & 2nd Stage CN TMT AMT (lbs)	1st & 2nd Stage CN TMT Cost
Sulfuric Acid				
2nd stage CN tmt	—	—	<0.01	$0.01
Sodium Hydroxide				
1st stage CN tmt using Cl_2	1.09	$0.16	—	—
1st & 2nd stage CN tmt using Cl_2	—	—	2.70	0.41
1st & 2nd stage CN tmt using NaOCl	—	—	0.28	0.04
Chlorine				
1st stage CN tmt	0.96	0.25	—	—
1st & 2nd stage CN tmt	—	—	2.38	0.63
Sodium Hypochlorite				
1st stage CN tmt	1.00	0.60	—	—
1st & 2nd stage CN tmt	—	—	2.50	1.50

Table 11
Treatment Costs
1 Gallon Cyanide Plating Bath

Plating Bath	1st Stage Using Cl_2	1st Stage Using NaOCl	2nd Stage Using Cl_2	2nd Stage Using NaOCl
CuCN	$0.25	$0.36	$0.63	$0.94
ZnCN	0.21	0.31	0.54	0.80
Cd	0.41	0.60	1.05	1.55

Table 12
Zinc Bath (Chloride)-Make Up

Formula	Conc. (oz/gal)	Cost/Gal
$ZnCl_2$	14.0	$0.63
KCL	27.0	1.27
Boric Acid	4.0	0.11
Brighteners	10 ml	0.01
	Total Cost/Gallon	$2.02

lime is used, the excess required will be much more significant, especially when the sludge accumulation factor is considered. Table 16 shows actual sodium hydroxide consumption figures for three bath formulations given previously.

While considering real treatment costs the reader must not overlook the costs associated with the disposal of acids and alkaline solutions. Table 17 presents a chart that the reader can use to calculate these costs that are often neglected. The table provides data concerning the amount of caustic or lime required to neutralize 100 pounds of the acids most often used in metal finishing. The table can also be reversed to estimate the acid required to match an alkaline dump. Because of the variability of this aspect of metal finishing, no cost figures are given and each reader can use this chart to figure his own real costs for this portion of waste treatment. These costs can frequently be associated with disposal of alkaline cleaners and acid pickles that are unnoticed in most discussions of waste treatment.

Many shops try to offset the treatment costs by dumping pickles and cleaners simultaneously. While this practice has merit, it would be even better if the dumps were not made at all, or at least on a less frequent basis. Skimming, filtration, ultra-filtration, and reconstitution of cleaners have all shown merit in this regard. Electrolytic removal of metals from pickles has been successful, particularly with easy-to-plate metals. Theoretically a pickle would last forever if the dissolved metal could be removed on a continuous basis. Dragout, of course, requires replenishment and organic contamination could interfere with surface preparation; but the individual should consider the merits of this idea (and others) if acid consumption and related caustic costs are high.

Ion exchange, in some cases has been cost effective; but

Table 13
Acid Copper Bath-Make Up

Formula	CONC.	Cost/Gal
$CuSO_4 \cdot 5H_2O$	28 oz/gal	$1.10
H_2SO_4	7 oz/gal	0.60
Brightener	30 ml	0.06
	Total Cost/Gallon	$1.76

Table 14
Nickel Bath
Make Up

Formula	Conc.	Cost/Gal
$NiSO_4 \cdot 6H_2O$	35 oz/gal	$2.41
$NiCl_2 \cdot 6H_2O$	10 oz/gal	$1.01
Boric Acid	5.5 oz/gal	$0.15
Brightener	40 ml/gal	$0.11
	Total Cost/Gallon	$3.68

Table 15
Theoretical Consumption (lbs) Of Alkalies For The Precipitation Of Heavy Metal Per Shift

	Heavy Metal To Be Precipitated				
Alkali	**Cu**	**Ni**	**Cr**	**Zn**	**Cd**
$Ca(OH)_2$ (Cost)	7.60 ($0.23)	11.91 ($0.36)	25.22 ($0.76)	6.96 ($0.21)	3.16 ($0.09)
NaOH (Cost)	4.56 ($0.68)	7.04 ($1.06)	14.97 ($2.25)	4.08 ($0.61)	1.84 ($0.28)

Metal Hydroxide Formation
(Neutralization)

$$M^{+2}L^{-2} + Ca(OH)_2 \rightarrow M(OH)_2 + CaL$$
$$M^{+2}L^{-2} + NaOH \rightarrow M(OH)_2 + Na_2L$$

Table 16
Treatment Cost Per Shift
At 1 Gallon Per Hour Dragout
Non Cyanide Plating Solution

Type of Plating	Treatment Chemical	Amount lbs.	Cost
Acid Copper	**Sodium Hydroxide**	**7.44**	**1.12**
Nickel	**Sodium Hydroxide**	**12.0**	**1.84**
Zinc	**Sodium Hydroxide**	**8.0**	**1.20**

regeneration chemicals and associated costs, as well as any added treatment costs must be considered before leaping to a conclusion. If the reader is using ion exchange to produce high purity water for final rinses, printed circuit fabrication and the like, he should make a careful analysis of regeneration rates, acid and caustic use, and the waste treatment cost impact. High volume DI water users are often surprised or shocked by the true cost figures.

Table 17
Theoritcal Consumption (lbs) Of Alkalies For The Neutralization Of 100 lbs Of Acid

	Acid To Be Neutralized				
Alkali	**H_2SO_4 (Conc)**	**HCL 35%**	**HNO_3**	**HF**	**H_3BO_3**
$Ca(OH)_2$ (Cost)	76 ($2.28)	36 ($1.08)	59 ($1.77)	185 ($5.55)	180 ($5.40)
NaOH (Cost)	82 ($12.30)	39 ($5.85)	64 ($9.60)	200 ($30.00)	194 ($29.10)

Table 18
Sludge Volume and Disposal Cost Per Shift At 2% Solids (Wt.)

Type of Plating	NaOH TMT (gal)	Disposal At 0.40/gal	$Ca(OH)_2$ TMT (gal)	Disposal At 0.40/gal
Acid Cu	33.1	$13.24	53.8	$21.52
Cyanide Cu	11.8	4.72	17.0	6.80
Nickel	49.2	19.68	63.8	25.52
Chromium	77.0	30.80	110.9	44.36
Acid Zn	30.6	12.24	44.2	17.68
Cyanide Zn	10.2	4.08	14.9	5.96
Cadmium	10.6	4.24	15.4	6.16

Table 19
Sludge Volume and Disposal Cost Per Shift At 10% Solids (Wt.)

Type of Plating	NaOH TMT (lbs)	Disposal At 0.10/lb	$Ca(OH)_2$ TMT (lbs)	Disposal At 0.10/lb
Acid Cu	55.4	$5.54	89.4	$8.94
Cyanide Cu	20.0	2.00	28.0	2.80
Nickel	82.7	8.27	105.4	10.54
Chromium	128.4	12.84	184.8	18.48
Acid Zn	51.4	5.14	73.4	7.34
Cyanide Zn	16.7	1.67	25.0	2.50
Cadmium	17.3	1.73	25.4	2.54

There are some treatment costs that are difficult to establish with scientific precision. These uncertainties pertain mostly to additives that are pace-fed into the waste stream. Perhaps the most important of these is the polyelectrolyte flocculating agents that should be used in *all* wastewater systems. The dose rate is normally established on the basis of flow and amounts to only a few parts per million. As a consequence of this low application rate, most waste treatment systems require only a few dollars ($1 to $5) per shift for this material.

Other additives that may be required to achieve particularly low metal levels, remove fluoride, oils and grease, detergents and complexing agents, and can also add substantially to chemical treatment costs. Here again the moral of the story is to minimize the release of these substances to the waste streams. For example centrifugal "chip wringers" can literally pay for themselves by salvaging

Table 20
Sludge Volume and Disposal Cost Per Shift At 20% Solids (Wt.)

Type of Plating	NaOH TMT (lbs)	Disposal At 0.10/lb	Ca(OH)₂ TMT (lbs)	Disposal At 0.10/lb
Acid Cu	27.4	$2.74	44.7	$4.47
Cyanide Cu	10.4	1.04	14.6	1.46
Nickel	41.4	4.14	52.7	5.27
Chromium	64.1	6.41	92.1	9.21
Acid Zn	25.4	2.54	36.7	3.67
Cyanide Zn	8.8	0.88	12.7	1.27
Cadmium	8.7	0.87	12.7	1.27

Table 21
Sludge Volume and Disposal Cost Per Shift At 30% Solids (Wt.)

Type of Plating	NaOH TMT (lbs)	Disposal At 0.10/lb	Ca(OH)₂ TMT (lbs)	Disposal At 0.10/lb
Acid Cu	18.7	$1.87	30.7	$3.07
Cyanide Cu	6.7	0.67	9.3	0.93
Nickel	27.4	2.74	35.4	3.54
Chromium	42.7	4.27	61.4	6.14
Acid Zn	17.3	1.73	24.7	2.47
Cyanide Zn	5.3	0.53	8.4	0.84
Cadmium	6.0	0.60	8.7	0.87

Table 22
Sludge Volume and Disposal Cost Per Shift At 40% Solids (Wt.)

Type of Plating	NaOH TMT (lbs)	Disposal At 0.10/lb	Ca(OH)₂ TMT (lbs)	Disposal At 0.10/lb
Acid Cu	14.0	$1.40	22.7	$2.27
Cyanide Cu	5.5	0.55	7.3	0.73
Nickel	20.7	2.07	26.7	2.67
Chromium	32.0	3.20	46.0	4.60
Acid Zn	12.7	1.27	18.7	1.87
Cyanide Zn	4.0	0.40	6.0	0.60
Cadmium	4.7	0.47	6.7	0.67

Table 23
Treatment Costs For 8 Hrs At 1 G.P.H.D.O. (NaOH Used For Neutralization)

Plating Bath	Make Up Cost	Treat Cost	Disposal Cost At 30% Solids	Total Cost
Cu	$14.08	$1.12	$1.87	$17.07
CuCN	11.92	7.87	0.67	20.46
Ni	29.44	1.84	2.74	34.02
Cr	18.80	3.61	4.27	26.68
Zn	16.16	1.20	1.73	19.09
ZnCN	8.16	7.31	0.53	16.00
Cd	8.88	12.86	0.60	22.34

oil from parts and keeping it from contaminating cleaners and rinses. Similar attitudes regarding other troublesome materials can lead to significant savings, reduced operating costs and less sludge disposal problems.

Now that the chemical costs of wastewater treatment have been reviewed, we are now in a position to cover the very important, often troublesome, and usually expensive aspect to pollution control, namely solids management and disposal. In some cases suspended metals and metal hydroxides must be removed from the effluent prior to release to the sewer or stream. The only exceptions are those small platers with flows under 10,000 GPD and who have no lead or cadmium in the discharge. In many locations even these platers are required by state or local codes to remove suspended metallics.

At the 10% solids content the sludges resemble toothpaste in consistency and are usually generated by centrifuging the pea-soup sludges of 2 to 5% solids content. It is possible to approach 20% solids content with small centrifuges particularly if the heavy metal content is really heavy, as for example, lead hydroxide. Keep in mind that the centrate or liquid discharge is not clarified and needs reprocessing (or repeated recycling). Experience and good engineering as well as a good centrifuge are required to make a trouble free installation. If the sludge has a high lime or abrasive content (from tumble finishing), the bearings, scoops, etc., may exhibit serious wear. It is therefore incumbent upon the user or his consultant to "know" his sludge before making a commitment to purchase any dewatering equipment.

Table 20 shows the effects of 30% solids content on disposal costs. In the progression from 2% to 30% there has to be a steady and dramatic reduction in costs, while the equipment costs have been relatively constant. A small 100 psi, recessed plate, pressure filter can be purchased for a little more than a comparable centrifuge, and probably for less than a vacuum filter. Here again a semi-granular sludge can be dewatered more efficiently and actually produce solids levels of 35% or better. Of course the filter must be sized to match the sludge accumulation rate, and large filters can be quite expensive. Automation and safety features such as light curtains, interlocks etc., can raise the prices further. Care must be exercised in pressure filter selection to assure a proper match to a particular situation.

High pressure filtration using recessed plate filters with 200 psi or higher feed pressures will produce even drier sludges, usually in the range of 35 to 50% solids.

Table 22 shows how these filters could effect disposal costs. While these filters are more expensive than the lower pressure types, high accumulation rates and/or long distance disposal could easily justify the added expense.

Table 23 presents a consolidated overview of wastewater treatment costs from the initial investment in the plating bath make-up through final sludge disposal of a nominal 30% solids content. Notice that this paper has not considered waste treatment systems costs, depreciation factors, operator salaries, power requirements (costs), maintenance costs and the like. Obviously the figures will relate to the size and complexity of the effluent treatment system and impact upon the figures presented here. If the reader takes the time to add these costs to the ones presented he will obtain a true, bottom line for the cost of wastewater treatment, and perhaps generate sufficient motivation to initiate conservation and/or recovery programs.

The technology of suspended solids removal is well documented and covers a variety of methods ranging from circular clarifiers and rectangular settling tanks to tube and lamella settlers. Regardless of the technology and equipment employed, the common factor is the sludge produced while clarifying the effluent. Without special thickening devices the sludge produced will range from 0.5 to 2% solids; but with thickening, the solids content could be as high as 5 to 7%. Table 18 shows the sludge volume and disposal costs at 2% solids for a single eight hour shift using the one gallon per hour drag-out rates previously developed. It is readily seen that these costs with sodium hydroxide use are very high and with the use of lime are further elevated. The fact that lime is seldom as efficient as theory would predict results from its limited solubility and its deactivation by fluorides, sulfates, oils and grease. Lime must therefore be applied in excess of theory and increased sludge volumes result. It is important to consider this factor, as well as initial cost, whenever contemplating the use of lime in wastewater treatment.

The cost of diposal of sludges at the two percent solids concentration will obviously be unacceptable to all but very small generators with low sludge accumulation rates. For those with higher generation rates, compaction of some sort must be employed. There are a variety of dewatering methods available to the finisher and each application must be judged on a case-by-case basis. The cost of the dewatering equipment, operating costs, maintenance, and anticipated disposal costs based upon expected generation rates at any given solids content must be considered in the selection process. It would be wise to check with local haulers and disposal sites concerning any limitations with respect to solids (or moisture) content. In some places sludges with less than 25% (or 30, or 35%) solids are not acceptabie. It would be an unfortunate error to select a dewatering device that could not produce a proper solids content for the disposal location selected.

The effects of raising the solids content to only 10% are shown in Table 19. There is an obvious and dramatic reduction in disposal cost. If the reader's costs do not correspond with those presented, it would not be difficult to adjust the figures to correspond to local conditions. The ten cents per pound may be somewhat high for the present. A survey of actual costs showed that many haulers charge by the pound or ton, then add a mileage and disposal fee for each load. In a number of cases the combined cost came to about 7.5 cents per pound ($150.00 per ton), as compared to quotes of 60 to 100 dollars per ton, without mention of the "extras". The haulers also indicated that their prices would go up as fewer disposal sites were available, and hauling distances increased. On this basis, 10 cents per pound makes an easy figure to work with, while not being entirely unrealistic.

The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

Energy, Environmental and Safety Benefits Through Computer Controlled Curing Oven Processes

Wilbur F. Chinery and Stephen J. Ansuini*

INTRODUCTION

It is not often we set out to reduce energy costs and achieve it along with higher air quality being exhausted to the atmosphere. These items though most often inversely proportional have proven to be the exceptions rather than the rule in this project. This project came about as a cooperative effort between private industry and the U.S. Government. The Environmental Protection Agency's Industrial Environmental Research Laboratory along with the Department of Energy's Office of Industrial Programs worked with the Chemical Coaters Association; Centec Corporation's Process System Group, an engineering firm applying microcomputer technology to the manufacturing industries with offices based in Ft. Lauderdale, Fla.; and Mack Trucks, Inc., a manufacturer of heavy duty trucks with offices based in Allentown, PA.

The demonstration was carried out in our Small Parts Paint Building (SPPB) at our Allentown Assembly Plant. The building, 106,500 sq. ft., contains four separate paint systems, an eight stage zinc phosphate washer, four elevated ovens and the necessary supporting equipment. Figure 1 shows the functional diagram of the SPPB's four ovens and incinerator operation. The color and prime ovens are spray paint ovens where parts receive one of three modes of paint application: conventional spray, airless spray, or electrostatic spray. The color, prime and dip oven (CPD) exhausts are combined at the CPD exhaust fan then passed through an auxiliary heating coil and sent to the catalytic incinerator for Volatile Organic Compound (VOC) destruction. After passing through the catalytic bed the gases can pass through or by-pass an air-to-air heat exchanger, which provides the necessary heat for the fourth oven, operating at 350° F. This is the only heat source for the electrodeposition ("E"-Coat) curing oven.

BENEFITS

Oven air-flow control technology extends to us several benefits:

Environmental
- —Utilizes recovered heat effectively
- —Assures 90% destruction efficiency

Energy
- —Reduces operating costs of ovens
- —Reduces operating costs for incinerator control equipment by 10 to 55%
- —20% investment tax credit (at time of writing)

Other
- —Safer operation by several orders of magnitude than uncontrolled systems
- —Expandable to 3-oven and one incinerator control

ECONOMICS

"The curing processes are energy intensive and usually account for more than 50% of the total manufacturing energy. Significant energy losses occur because of venting from the curing ovens"[1] caused by high dilution air flows. The payback period and the investment amount would be highly dependent on air flow rates, solvent removal rates and system configuration. However the Discounted Cash Flow (DCF) rate of return and payback have shown

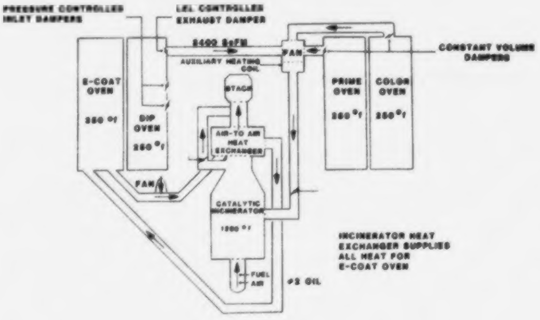
PRESSURE CONTROLLED INLET DAMPERS
LEL CONTROLLED EXHAUST DAMPER
2400 ScFM
FAN
CONSTANT VOLUME DAMPERS
AUXILIARY HEATING COIL
E-COAT OVEN
350 °F
DIP OVEN
250 °F
STACK
PRIME OVEN
250 °F
COLOR OVEN
250 °F
AIR-TO AIR HEAT EXCHANGER
FAN
CATALYTIC INCINERATOR
1300 °F
FUEL
AIR
#2 OIL
INCINERATOR HEAT EXCHANGER SUPPLIES ALL HEAT FOR E-COAT OVEN

Fig. 1—Functional diagram of SPPB 4 Ovens and Incerator System.

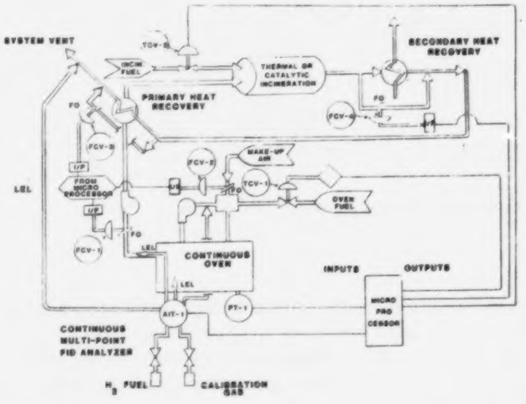
SYSTEM VENT
TCV-2
INCIN FUEL
THERMAL OR CATALYTIC INCINERATION
SECONDARY HEAT RECOVERY
PRIMARY HEAT RECOVERY
FO
FO
FCV-4
FCV-3
MAKE-UP AIR
FCV-2
I/P
LEL
FROM MICRO PROCESSOR
TCV-1
FO
OVEN FUEL
I/P
FO
FCV-1
LEL
CONTINUOUS OVEN
INPUTS
OUTPUTS
LEL
AIT-1
PT-1
MICRO PRO CESSOR
CONTINUOUS MULTI-POINT FID ANALYZER
H2 FUEL
CALIBRATION GAS

Fig. 2—Control System Operation Flow.

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[1] DOE Tech. Briefing Report, "Oven Curing: Energy and Emission Control in Coil Coating," TID-28705, 1978.

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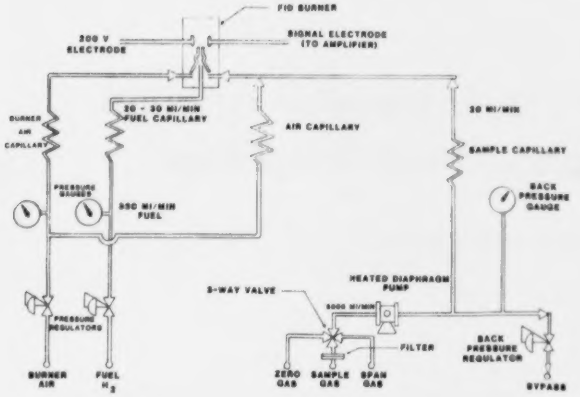
FID BURNER
200 V ELECTRODE
SIGNAL ELECTRODE (TO AMPLIFIER)
BURNER AIR CAPILLARY
20 - 30 MI/MIN FUEL CAPILLARY
AIR CAPILLARY
30 MI/MIN
SAMPLE CAPILLARY
PRESSURE GAUGES
350 MI/MIN FUEL
BACK PRESSURE GAUGE
HEATED DIAPHRAGM PUMP
3-WAY VALVE
5000 MI/MIN
FILTER
BACK PRESSURE REGULATOR
PRESSURE REGULATORS
BURNER AIR
FUEL H_2
ZERO GAS
SAMPLE GAS
SPAN GAS
BYPASS

Fig. 3—Typical Fid Analyzer Detection Unit Flow Diagram.

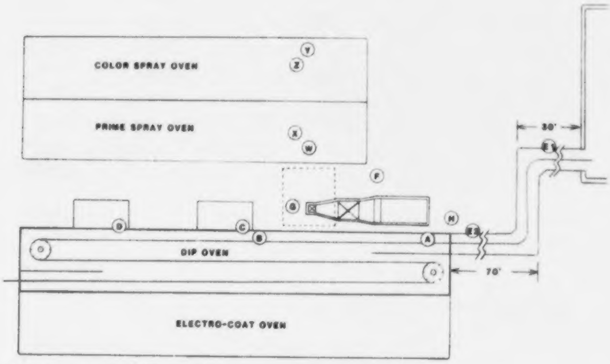
COLOR SPRAY OVEN
Y
Z
PRIME SPRAY OVEN
X
W
30'
F
G
H
D
C
B
A
DIP OVEN
70'
ELECTRO-COAT OVEN

Fig. 4—Overhead View with Sample Points Indicated.

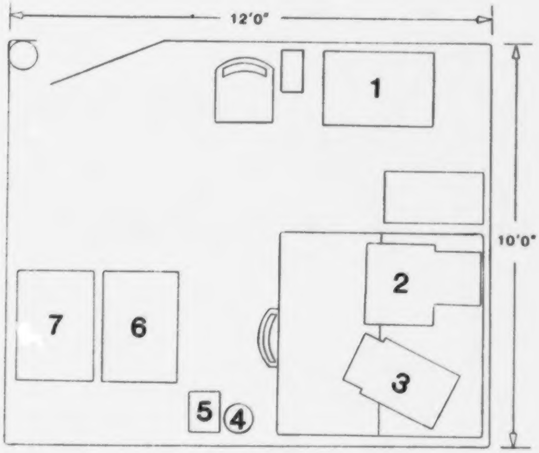
12'0"
10'0"
1
2
3
5
4
6
7

Fig. 5—Equipment Room SPPB Mack Trucks, Inc.

favorable figures when dealing with paper, fabric, wire, coil and other coaters involving high air flow rates.

We at Mack are working with one oven with a low flow rate, 3400 scfm, and have successfully reduced it by 85%. The dip oven exhaust now measures 400 to 500 scfm. With this reduction of cooler dilution air we have cut previously required Btu's to maintain oven temperature substantially

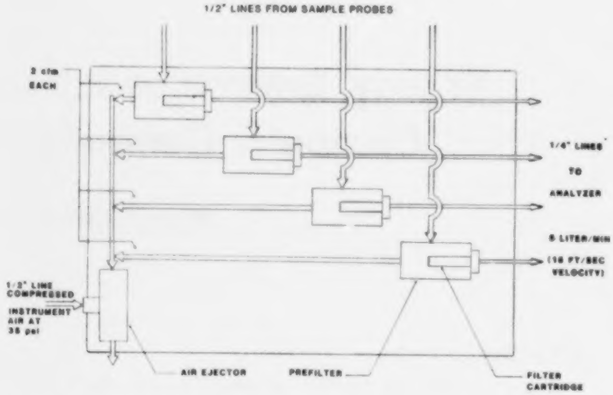
1/2" LINES FROM SAMPLE PROBES
2 cfm EACH
1/4" LINES TO ANALYZER
5 LITER/MIN (16 FT/SEC VELOCITY)
1/2" LINE COMPRESSED INSTRUMENT AIR AT 35 psi
AIR EJECTOR
PREFILTER
FILTER CARTRIDGE

Fig. 6—Self-Cleaning Prefilter Station.

It is estimated conservatively we are realizing a $26,000 annual savings on fuel. The reduced air flows would allow for incinerator down-sizing providing still another savings.

COMPUTER CONTROL SYSTEM

Purpose: Automatic and continuous control of the dilution air flow into the curing oven and other tasks like monitoring and logging essential information are just a few of the computer's duties.

We began by sketching a control system operational flow diagram. It was imperative that we observed strict safety parameters at this point. The system should be capable of detecting: computer failures, high caution levels, high alarm levels, analyzer failures and power interruptions. Once the failure is detected, the system should act with fail safe precision. To achieve this the "what if" and the fault tree analysis were utilized. Figure 2 shows a basic control system. In addition to the Lower Explosive Limit (LEL) Analyzer (AIT-) and micro-computer hardware, the dilution air-flow control system includes temperature (TCV-), and pressure (PT-), automatic dampers with pneumatic actuators (FCV-) and actuator controls (I/P). The I/P units take an electrical signal from the computer, interpret it, and provide a proportional pneumatic pressure to the actuator.

Safe operation of the system is dependent on the sensitivity, reliability, and stability of the VOC vapor/LEL Analyzer. A multi-point Flame Ionization Detector (FID) Analyzer was selected for the control system. Figure 3 is a typical FID Analyzer Detection Unit flow diagram. The FID burner receives hydrogen gas as its fuel, combustion air and the sample gas. Prior to injection, air is added to the sample gas to ensure complete combustion of the sample. Within the FID burner are two plates separated by the combustion area. One plate is at a 200v potential and the other is the signal input to a high gain amplifier. As the sample gas is burned it allows the signal plate to pick-up a signal which is directly proportional to the amount of VOC's present. Other controls allow the introduction of zero gas and sample gas for calibration needs.

The control room location was also a point of consideration. It was necessary to minimize the sample line runs outside the oven which required heated lines and to be centrally located for the color, prime, dip ovens and the incinerator. For this reason it was positioned below the incinerator exhaust stack as indicated in Figure 4 by the dotted line around sample point "G". A 10 ft × 12 ft modular

Table 1

Analyzer, AIT-1:	Metal Prefilter	Bypass Type	Process Temp.	Heated Line
A Primary D.O. Air Seal	Yes	Yes	250°F	Yes
B D.O. Exhaust	Yes	Yes	250°F	Yes
C D.O. Zone 1	Yes	Yes	250°F	Yes
D D.O. Zone 2	Yes	Yes	250°F	Yes
E Fume Tunnel Exhaust	No	No	85°F	No
E Fume Tunnel Exit	No	No	85-220°F	No
E^1 Fume Tunnel Auxillary	No	No	85-220°F	No
F^2 CPD Combined/Incin. Inlet	Yes	No	220°F	Yes
G Incin. Exhaust	Yes	No	600°F	Yes
H Ambient	No	No	85°F	No
Analyzer, AIT-2:				
W P.O. Product Inlet	Yes	Yes	250°F	Yes
X P.O. Exhaust	Yes	Yes	250°F	Yes
Y C.O. Product Inlet	Yes	Yes	250°F	Yes
Z C.O. Exhaust	Yes	Yes	250°F	Yes

D.O. — Dip-Coat Oven P.O. — Prime Oven C.O. — Color Oven

enclosure proved neessary as indicated by Figure 5. Item one is a four channel FID Analyzer (Ratfisch), two - an Omni-800 printer (Texas Instrument), three - color video terminal (ICS), four - 8,000 parts per million (ppm) methane in nitrogen calibration gas, five - a Mark V hydrogen generator 300 ml/min. (Milton Roy), six - the cabinet houses the heart of the control system an Intel 8080 microprocessor and interfacing hardware, seven - an eight channel FID Analyzer (Ratfisch).

The video display gives necessary data to the viewer and includes the date and time, percent LEL for eight sample points and a normal/failure indication on four other LEL points in the color and prime spray ovens; temperature information and pressure information on the dip oven; temperature levels in the fume tunnel, incineration inlet, pre-catalyst and post-catalyst; destruct efficiency and percent open of the dip inlet and exhaust dampers; alarm horn enable switch on/off; and whether the system is in a monitor mode or control mode (auto). The bottom of the screen provides information to the inquirer as to those items that may be accessed. By knowing a password the operator can make some control level changes as long as they fall within the pre-programmed limits. A graphical display may also be employed at the discretion of management.

Figure 4 shows sample point locations as originally proposed and how they were installed. As this was the first system of its kind in the world, we exercised extreme caution and sampled more points than we now feel were necessary for our particular application. Table 1 shows a breakdown of the sample points indicating four parameters of importance. The heated sample lines are necessary to maintain sample integrity by preventing condensation from occurring in the lines. They are adjusted at the FID Analyzer to the oven operating temperature and controlled thereafter by the Ratfisch electronics package. Each sampling probe was locally fabricated at a substantial savings over purchasing manufactured ones. A length of stainless steel ½ in. or ¼ in., dependent on type, was capped and a series of small holes were equally spaced across the duct opening. The number of holes were calculated to allow the same flow as the tube size. All sample lines that were routed through a self-cleaning prefilter station, shown in Figure 6, were run using half inch stainless tubes to the filter and a ¼ in. was then fed from each filter to the oven floor where transition was made to a heated sample line.

Figure 6 shows the self-cleaning prefilter station. The draw on the four filters is provided by an air eductor (ejector). Supply instrument air is at 35 psi and each filter has a flow of 2 cfm. The analyzer pump pulls only 5,000 ml/min from each filter line, and of that only 20 ml/min is used by the FID for analysis. This method of sampling provides minimum reaction time to LEL changes within the oven. In our application this is not as critical, as we are looking at a 30 minute residence time of our parts, but would be critical for a coil coater working with seconds for residence time.

CONCLUSION

The potential benefits of this control technology have long been under investigation. For the miscellaneous metal products coating industry alone, fuel savings would be substantial. Product lines in this industry include office furniture, major and small appliances, industrial cabinets and partitions, toys, kitchen utensils, lawn furniture and other small metal products.

There are approximately 6,000 of these ovens in operation in one thousand plants across the country. If this control technology were applied to 10% of the ovens mentioned above, the 600 ovens have a potential annual savings equivalent to 1.5 million barrels of oil. If each of these ovens had an incinerator for VOC control the annual savings would increase to 6.8 million barrels of oil.

It is important to look at the LEL levels at the reduced air flows. As we discovered it may not always be necessary to have a controlled system even when reducing air flows 85%. A continual monitor with alarm levels may save a great deal of front end costs. The initial field surveys are critical and more attention should be given to this important foundation.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

Oily Wastewater Treatment By Electrochemical Techniques

Delia M. Yarema*

This paper will discuss The Stanley Works proposed project to treat oily wastewater by an electrochemical technique patented by the Ford Motor Company. The reasons for the selection of this method and the anticipated benefits will be featured.

The Stanley Works is a major manufacturer of builders hardware, hand tools and fabricated metal products. I am sure you will all recognize our Corporate slogan - STANLEY HELPS YOU DO THINGS RIGHT. In environmental areas, Stanley shares the feeling of all metal finishing industries represented here today in trying to do things right with respect to pollution abatement. However, finding economically attractive technologies that can be practically applied on a day-to-day basis is a constant problem.

The Stanley Works Corporate Headquarters is located in New Britain, Connecticut. Within this complex are many Stanley divisions and Corporate support groups. Wastewater generated from manufacturing operations is discharged to twenty-six separate sanitary sewer connections. To insure compliance with State and local discharge regulations, an intensive wastewater discharge assessment program was conducted in 1979. This survey identified oil/grease discharges requiring additional treatment to bring them within the Publicly Owned Treatment Works (POTW) limit of 100 mg/l. One of the systems identified as a problem area was the discharge from an American Petroleum Institute (API) separator within the Hardware Division.

The API separator accepts a maximum of 45,000 gpd of oily wastewater from industrial washers located in Building 150. Manufacturing operations include rolling, broaching, tapping, drilling, counterboring and stamping. Before parts are stored, plated, or painted, residual oil, dirt, and metal chips are removed in the industrial washing machines. In some cases, parts must be washed between successive manufacturing operations. Since the metalworking operations require lubricants with diverse properties, the oils used range from chlorinated compounds to heavily pigmented materials. This complex waste stream flows to the API separator where free oil is removed. However, the resulting wastewater discharge still contains approximately 1000 mg/l of emulsified oil.

A combined task force of Corporate facilities engineering, Corporate laboratory, and manufacturing personnel reviewed the entire operation to assess the extent of the problem. Guidelines were established to streamline the number of lubricants presently in use. This is still an ongoing process since a change in lubrication must be carefully evaluated with respect to lubricity, tool and die life, ease in cleaning, and protection against rust in storage. Wherever possible, flow restrictors and solenoid valves are utilized to reduce the volume of water. The use of cleaners that split out oil have reduced the load on the API separator. However, after all these modifications the waste stream requires treatment prior to discharge to the sewer.

In determining the method of treatment to be used for this waste stream some basic factors were extremely important.

1. We needed to produce treated water of a quality that would be both acceptable for discharge to the sanitary sewer and for future re-use as make-up water for the industrial washers. With proposed sewer taxes and the probability of future water shortages, the continuation of draining to sewer was at best a temporary solution.
2. The treatment method must handle a waste stream variable in oil concentration, surfactant level, and particulate contamination with reliable results.
3. The system must be fully automated and require a minimum of operator attention.
4. The system must be cost effective with respect to capital and operating expense.

Initially, the following processes were considered for the removal of emulsified oil from this waste stream:

1. Conventional Chemical Treatment,
2. Colloid Piepho System RP,
3. Ultrafiltration, and
4. High Speed Centrifuge.

Conventional Chemical Treatment utilizes acid and inorganic chemicals to break the emulsion. If we chose to pursue this treatment method, we would have to abandon our idea of re-using the water unless a demineralizer was placed on the return water line. Acid and inorganic chemicals would allow the continual build-up of dissolved solids which could result in corrosion problems with product going to storage. Conventional treatment is best suited to a batch type operation as opposed to continuous treatment and normally it requires intensive floor space. Chemical treatment costs would be approximately 85¢/1000 gallons of water treated. Conventional chemical emulsion breaking could also be done with polymers. Polymer dosage normally ranges between 1000/2000 ppm with costs approaching $1/1000 gallons of water treated. Because of the high chemical treatment costs, it was decided

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to review alternative methods for treating the oily wastewater with conventional treatment as a last resort.

A plant trial was conducted utilizing a Colloid Piepho System RP. Colloid Piepho supplies a proprietary multifunctional chemical to be used with their equipment. This chemical is a clay type material which appears to sorb the emulsified oil. The resultant sludge is dewatered utilizing a moving paper filter. Although effluent oil analyses were less than 25 mg/l, the inherent operating costs of the system proved unacceptable. Chemical costs were estimated to range between $25,000 and $50,000 per year with a capital cost for an automated system at $75,000. Additional costs would include the paper for the filter and transportation and handling charges for removal of the sludge from the plant property. Since solid waste landfills in Connecticut are approaching capacity levels, we could be building into the system an escalating disposal cost.

A third option for treatment of the emulsified wastewater was Ultrafiltration. Ultrafiltration is a low pressure membrane process to separate the emulsified oil from the wastewater. As the wastewater flows across the membrane, water and low molecular weight materials pass through the membrane and are collected as permeate. Emulsified oil and particulate matter are retained by the membrane. In this way the oil can be concentrated to between 50-60%. Performance of the system is optimized by the removal of free oil and readily settleable solids. Membrane flux (gfd of permeate) can be affected by temperature, concentration of free oil in the wastewater, and the fouling rate of the membrane. Laboratory experimentation indicated that some of the surfactants involved in either the basic formulation of the lubricant or cleaning chemicals can pass the membrane. These materials would then recirculate and concentrate within a re-use water system. Basic capital cost for the ultrafiltration system was $175,000. We were aware that replacement membrane cost could run as high as 25% of the capital cost every four to five years.

Brief Laboratory studies indicated that a High Speed Centrifuge (13,000 g's) was not effective in breaking the emulsion. This treatment concept was therefore abandoned.

In our review of the available treatment methods, it became apparent that no one system would satisfy all of our needs in a cost effective manner. Through the EPA Research Laboratory in Cincinnati, we learned of a process developed by the Ford Motor Company which treats oily wastewater by electrochemical means. Ford held patents on the process and had developed a 1500 gpd pilot unit at their Lavonia, Michigan Transmission Plant. The pilot unit was treating oily wastewater from diverse machining operations similar in nature to those done within the Hardware Division of The Stanley Works. The wastewater contained emulsified oils, surfactants, and tramp oils as well as occasionally being contaminated with hydraulic oils, drawing compounds and transmission fluids. As with the waste stream in our plant, Ford's waste stream changed frequently in composition. However, initial results published by Ford indicated that they were able to treat oily wastewater containing from 300 to 7000 mg/l of oil/grease to less than 50 mg/l in 90% of their trial work. This treatment level is well below the 100 mg/l discharge limit to our sanitary sewer and would be totally acceptable for re-use water characteristics.

Our initial contacts with the EPA and the Ford Motor Company generated extreme interest on the part of The Stanley Works to obtain more information about this system. The Ford Motor Company granted The Stanley Works a limited patent license to operate a treatment system within the New Britain Complex of The Stanley Works. Preliminary feasibility studies conducted in our Laboratory allowed us to reduce the oil content in our discharge by 99%.

The Ford System is a continuous process which employs a porous electrode that can be operated at a low voltage and low current to yield essentially oil-free water. Oily emulsion wastewater is collected in a flow equalization tank where free floating tramp oil can be removed utilizing a skimming device. The waste stream requires sufficient conductivity for cell operation and to prevent passivation of the iron electrode. In the Ford System, calcium chloride is added to the waste stream prior to entering the electrolytic cell. The cell is comprised of a caged bed of iron or steel machining chips which act as an anode with a perforated steel metal sheet as a cathode. Voltage is applied to the electrodes, dissolving ferrous ions at the anode and forming hydrogen and hydroxyl ions at the cathode. The ferrous ions react with the chemical oil-emulsifying agents, and with the addition of air are oxidized to ferric ions, further destabilizing the emulsion. The destabilized oil emulsion droplets sorb onto the dispersed and reactive ferric hydroxide floc. An oil-rich sludge is generated. In the Ford System, flotation is assisted by the introduction of microbubbles into the cell flotation section. A belt skimmer collects the sludge blanket while clear water overflows to a sand filter and then to a clean water tank.

Ford's research has shown that the oil content in the effluent has a direct relationship to turbidity. The system has been automated so that the signal from a turbidimeter controls the applied current. Ford's system normally operates at an average voltage of 20 with current ranging from 15-35 amps.

Stanley's proposed project would utilize a dissolved air flotation unit for sludge collection rather than an air bubbler flotation system. We do not anticipate the need for final polishing of the effluent and therefore would not employ a sand filter at this time.

Economic projections are favorable with an anticipated capital cost of $60,000. The major portion of this expenditure would be for a commercially available Dissolved Air Flotation (DAF) unit. Machining chips are readily available within the New Britain Complex as an iron source. The exact amount of chemical required for ionic conductivity still needs to be determined. We will investigate the possibility of utilizing a material that would not only increase the conductivity but also provide a corrosion inhibiting property to the water.

Operating cost is directly related to flow rate, current and type, and concentration of chemical. For a given influent composition and flow rate, the current determines the rate of iron dissolution and therefore the ratio of iron to oil. To operate the system at a minimum cost, this ratio must be kept as low as possible without sacrificing effluent oil quality. Work completed by Ford was directed towards obtaining an effluent oil concentration in the range of 10 mg/l.

Since we would not require this level of water quality, we anticipate our operating costs to be lower than the 68¢/1000 gallons that Ford has reported.

In our opinion, the practical demonstration of this process on a larger scale than Ford's 1500 gpd pilot unit is extremely important to the metal finishing industry. The electrochemical treatment method would allow for the re-use of the water, generate a minimal quantity of sludge rich in oil, while utilizing an available waste material (scrap steel) in the treatment process. We feel that this system is the best technology available for the resolution of our oily wastewater problem.

I would like to take this opportunity to thank the Ford Motor Company for their continued assistance in this project, particularly Dr. Marvin Weintraub for providing the slides of the electrochemical process utilized in this presentation.

We look forward to reporting to you at a later date the results of our project.

REFERENCES

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2. Weintraub, M. H. Gealer, R. L., "Development of Electrolytic Treatment of Oily Wastewater," Report Presented at American Institute of Chemical Engineers 1977.

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Cross Flow Filtration Technology For Metal Finishers

Han Lieh Liu and James Blacklidge*

INTRODUCTION

This paper presents the results of two wastewater treatment technology evaluation programs sponsored by the U.S. Environmental Protection Agency (U.S. EPA). These programs were concerned with the application of a microfiltration system designed to treat industrial wastes containing heavy metals. Major results of the first program, a lead-acid battery manufacturing wastewater study, have been published ("Removal of Heavy Metals and Suspended Solids from Battery Wastewaters: Application of Hydroperm Cross-Flow Microfiltration" EPA-600/S2-81-147). Additional data from the first program are provided in this paper. The second program concerned the use of a microfiltration system to treat electroplating wastewaters. The results from that study are the main subject of this presentation.

Conventional wastewater treatment technologies for the electroplating industry consist of physical and chemical processes for the destruction of cyanide, the reduction of hexavalent chromium to the trivalent state, and the neutralization/precipitation/clarification of heavy metals in wastewaters. Heavy metals are usally precipitated as their hydroxides. These metal hydroxides usually have low solubility and can be precipitated by adjusting the pH to an appropriate level; however, because some of these metals are amphoteric, the precipitation of these metals is not an easy task in the treatment of plating wastewaters.

The separation of precipitated solids has been a challenge to the metal finishing industry. Traditional separation techniques, such as gravity settling and centrifugation, are not totally effective since the precipitated solids are usually hydrous and have densities very close to that of water. In addition, the design of the required clarifier, in a number of instances, limits the retention time in the settling chamber due to size limitations. There is, therefore, a need to develop more compact alternative solid/liquid separation techniques for treating electroplating wastewaters.

In recent years, the use of cross-flow filtration has been broadly employed in various solid/liquid separation applications. In this process, the direction of the influent flow is parallel to the filter surface, while filtrate permeation occurs in a direction perpendicular to the flow. Examples of cross-flow filtration include membrane filtration techniques such as certain types of ultrafiltration (UF) and reverse osmosis (RO). The major disadvantages of membrane filtration systems include high energy consumption rates and low filtrate fluxes. The cross-flow microfiltration system, developed by Hydronautics under the registered name HYDROPERM®, shows the capability of removing suspended solids from wastewater with relatively low filtration pressure (1 kg/cm^2, 15 psi) while maintaining a reasonably high filtration rate.

As indicated, this paper presents the results of two field investigations ultilizing microfiltration (MF) in both an electroplating shop and a battery manufacturing plant. A general description of the cross-flow microfiltration technology is presented first. Field evaluation results are then presented.

Cross Flow-Microfiltration

In this process, a quasi-steady state operation is possible, since the continuous buildup of the separated solids on the filter surface is largely prevented by the hydrodynamic shear exerted by the circulation flow.

There are some fundamental differences in UF and RO systems and the microfiltration system. J. D. Henry, Jr. suggested[1] that microfiltration involves the retention of undissolved (particulate) material by the filtration barrier with tangential suspended flow while UF and RO involve the retention of dissolved species by the filtration barrier with tangential solution flow. In practice, this difference generally results in much higher filtration rates (flux) and lower energy requirements for microfiltration than for UF and RO.

Other significant physical and operational differences between UF, RO, and MF include filtration barrier wall thickness, pore size, liquid circulation velocity, and operating pressures. The typical UF and RO wall thickness is usually a few microns, whereas the MF wall thickness is approximately one millimeter. The pore size of UF and RO are less than one micron while MF pores are in the range of two to ten microns. The UF and RO liquid circulation rates are greater than 6 m/sec (20 ft/sec) while MF requires less than 2 m/sec (7 ft/sec). Finally, RO operates in the range of 42 to 84 kg/cm^2 (600-1200 psi) and UF operates in the range of 3.5 to 11 kg/cm^2 (50-150 psi). MF is usually operated at less than 1.4 kg/cm^2 (20 psi). The higher operational circulation velocities and pressures used for UF and RO systems are the results of the separation mechanisms involved.

In UF or RO, the fluxes are determined by a balance between convection of dissolved species proportional to the flux itself and back diffusion due essentially to molecular processes. This is true whether the tangential flow is laminar or turbulent. As the flux increases, the wall concentration due to polarization of filtered species increases (more rapidly for species of lesser diffusivity) until gelatin finally occurs. Thereafter, the gel layer grows until convection is balanced by back diffusion which is temperature dependent. As a consequence of the above process, during ultrafiltration the equilibrium flux is independent of filtration pressure beyond a certain pressure, and increases as the molecular diffusivity and wall shear (i.e., circulation velocity) increase.

In microfiltration, the fluxes are determined by

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Table 1
Permeate Quality During the Field Demonstration at CPT

Date	*Sample ID*	*pH*	*TS mg/l*	*TSS mg/l*	*Cd mg/l*	*Cu mg/l*	*Zn mg/l*	CN_T *mg/l*	Cr_T *mg/l*
5-28	C*	10.44	4030	2.0	0.4	0.1	0.1		
Sample 1	P1	11.25	4580	6.0	0.1	0.1	<.1	17.1	37.2
	F1	11.29	4960	408.0	44.0	1.5	7.6		
Sample 2	P2	10.54	2330	8.0	0.3	0.1	<.1		
	F2	10.44	7810	5530.0	1100.0	24.0	130.0		
5-29	S	10.66	12470	8796.0	2000.0	51.0	280.0		
6-1	P	10.30	5090	6.0	0.2	<.1	<.1	21.5	29.7
	F	10.28	12020	5940.0	1200.0	22.0	190.0		
	S	9.91	31450	25280.0	7000.0	106.0	720.0		
6-5	P1	9.60	4080	<0.1	0.4	1.4	<.1	10.1	35.2
Sample 1	F1	9.47	4750	4540.0	700.0	23.0	120.0		
Sample 2	P2	9.86	1900	<0.1	0.4	4.5	<.1	3.0	28.0
	F2	9.51	11740	9710.0	1600.0	37.0	240.0		
6-8	P	7.82	2620	<0.1	0.9	0.3	<.1		
	F	7.55	10890	8480.0	380.0	33.0	57.0		
6-10	C	12.37	4400	42.0	7.1	0.5	0.9		
6-15	P1	7.25	8420	65.3	132.0	3.8	0.3	0.6	<.1
	F1	7.14	12550	3610.0	460.0	17.5	22.0		
6-15	P2	6.11	5730	217.0	165	3.6	0.4	-	-
	F2	6.39	20000	14390.0	810	44.0	67.0	-	-
6-19	P1	9.60	6780	16.0	0.4	0.3	<.1	-	<.1
	F1	9.52	13230	6570.0	1200.0	100.0	100.0	-	-
	P2	9.59	5840	4.0	0.3	0.9	<.1	-	<.1
	F2	9.53	25640	17490.0	3200.0	310.0	260.0	-	-
6-29	P1	11.4	9677	14.0	0.1	0.2	0.1	-	-
	F1	10.8	8700	1240.0	250.0	11.7	30.0	-	-
	P2	10.5	6680	7.0	0.1	0.1	0.1	-	-
	S	10.4	12700	7500.0	1350.0	50.0	110.0		
6-30	S	9.37	16000	14430.0	-	-	-	-	-
7-6	P	10.48	14240	7.0	1.7	0.3	0.1	-	-
	F	10.98	26450	12310.0	-	-	-	-	-
7-7	S	10.68	11120	7160.0	-	-	-	-	-
7-12	S	9.93	12920	8780.0	-	-	-	-	-
7-21	P	9.95	1290	1.5	0.1	0.9	0.2	-	-
	F	9.88	3940	2530.0	-	-	-	-	-

*Taken after setting overnight from supernatant of clarifier.

C = Clarifier; P = Permeate; F = Feed; S = Sludge in the microfiltration recirculation tank (C is taken from supernatant of clarifier).

convection of particles (rather than dissolved species) proportional to the flux and the phenomenon which removes particles from the gel layer. With all environmental conditions being equal for comparative purposes, the cross-flow microfiltration of particles results in significantly larger fluxes than those noted during ultrafiltration of the dissolved species even though dissolved species have larger diffusivities.

Recently this solid removal mechanism in cross-flow filtration was reexamined by Tulin.[2] An erosion and deposition model was proposed. The model is analogous to the erodibility of sediment on the river bottom through the action of tangential flows (currents and waves). It is known that sedimentary materials are picked up from the river bottom when the tangential shear due to flow exceeds a threshold value. The material is subsequently carried in the direction of the current for a certain distance before being redeposited. Eventually, changes in the concentration of sediment in suspension reflect the net difference between rates of entrainment and deposition. The threshold value of shear stress, however, is dependent on the exact physical and chemical nature of the sediment (i.e. cohesiveness). The same types of erosion and deposition model can be applied to the cross-flow microfiltration system by adopting an additional variable, the permeation velocity. This mathematical model is still under investigation at this time.

The microfiltration technology results in a self-contained effluent clarification system that does not require the space, liquid flow, or retention time associated with typical clarification systems. The system used in these evaluations required a fraction of the space that normal clarification systems require to process the same effluent volume.

Field Evaluation

The microfiltration system filters used in the electroplating evaluation program were supplied by Hydronautics, Incorporated under the registered name, HYDROPERM®. The principal element of the system is a thick-walled (1 mm, 0.04 in), hollow tubular filter (6 mm ID, 0.24 in) made of thermoplastic material and containing micron-size pores.

The module, which was constructed for the full-scale system, contains eighty filter tubes in a 1.5 m (5 ft) long, 100 mm (4 in) diameter PVC pipe. The filtration surface area of one such module is 2.3 m^2 (25 ft^2). Four such modules, with a total surface area of 9.2 m^2 (100 ft^2) were arranged in parallel and in series on a skid base. Also mounted on this base were the feed circulation pump, permeate transfer pump, permeate holding tank, and clean solution tank. A 3.7

kW (5 hp) pump with a capacity of 681 lpm at 18 m head (180 gpm at 60 ft) was used to circulate the feed through the module system. The total system is pictured in Figure 1. This system is entirely self-contained. The only requirements for interfacing to the plating shop are the power line connection and feed line connection to the recirculation tank.

The Craftsman Plating and Tinning (CP&T) Corporation in Chicago was selected as the evaluation site for electroplating wastewaters. The plating processes are either barrel or rack. Metals plated are cadmium, copper, tin, tin-lead, and zinc. Special treatment in the shop include chromate conversion coating, etching, passivating pickling, hot solder dipping, and organic coating. The wastewaters (from dragout, rinse, spill, cleaning, etc.) flow to a common sump at a rate of about 7570 l/hr (2000 gal/hr). CP&T treats its wastewater with conventional processes including: cyanide destruction by chlorination; neutralization with caustic, suspended solids removal through clarification, and sludge thickening by centrifugation. The treated water goes to the city sewer. The flow diagram for the plant wastewater is shown in Figure 2. The microfiltration system was connected to the existing treatment facility at the neutralization tank discharge line. It was operated in parallel with the clarifier unit. A comparison of these two unit processes was therefore possible.

During the eight-week evaluation period, data were taken to determine permeate flux rates and permeate quality. The permeate samples were taken weekly and analyzed once per week by Scientific Control Laboratory, Incorporated, Chicago.

The feed to the microfiltration unit was the actual wastewater flow from the plant. It experienced a daily variation due to the type of plating conducted during the day. The associated pretreatment steps, cyanide destruction and neutralization, were adjusted accordingly. There were periods however, when the pH and cyanide destruction processes were not adequately controlled. During those times both the MF and the clarifier processes showed poor effluent quality. This result, however, was anticipated since the capability of both processes, MF or clarification, is dependent upon the success of the initial pretreatment steps.

Table 1 shows the microfiltration system performance during the field evaluation. Initial daily flux values were much higher than the corresponding plateau values, (i.e. steady state operating values) typically in the range over 24,450 l/m^2/day (600 gal/ft^2/day). The rate of decay of the flux values to plateau values during the day depends on feed wastewater characteristics. This in turn depends upon daily changes in the plating operations and subsequent changes in treatment. As a result, the suspended solids loading to the microfiltration system varied widely.

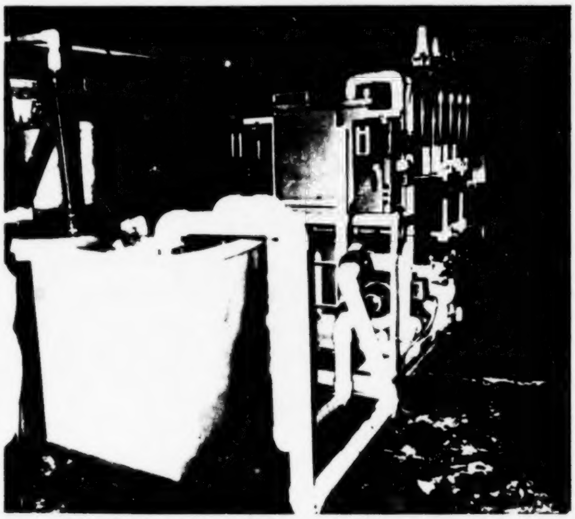

Fig. 1—Full scale HYDROPERM demonstration unit.

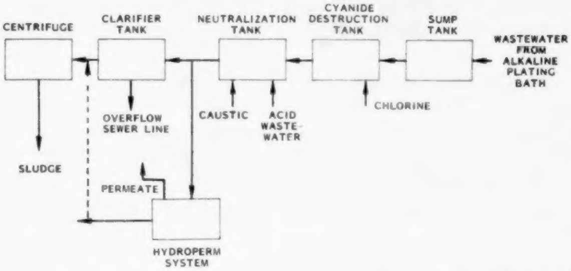

Fig. 2—Wastewater treatment flow diagram at Craftsman Plating and Tinning Corp.

In several incidences, there seemed to be no flux decline during the day. On other days, however, dramatic changes were noted; likely the result of poor physical and chemical control of the pretreatment steps. For example, during the June 15th run (see Table 1) the plateau flux was less than 2040 l/m^2/day (50 gal/ft^2/day) and the total solids (TS) in the permeate were abnormally high. The pH value that day was around 6 to 7, which was too low to effectively

Table 2
Laboratory Analyses on Metals in the Battery Wastewater Effluents

Date	*Samples*	*TS mg/l*	*SS mg/l*	*Pb mg/l*	*Cu mg/l*	*Zn mg/l*	*Ni mg/l*	*Sb mg/l*	*As mg/l*
2-27-80	Feed	162,740	160,000			54.5			
	Permeate	3,621	1.8	0.045	0.017	0.008	0.24	0.141	0.002
4-2-80	Feed	12,364	9,188	319.4					
	Permeate	3,378	1.0	0.029	—	—	—	0.151	<0.002
9-24-80	Feed	9,346	6,804	40.3					
	Permeate	2,773	1.0	0.082	0.023	0.024	0.053	0.058	0.003
11-11-80	Feed	11.932	9,180	55.2					
	Permeate	3,356	6	0.073	0.015	0.016	0.041	0.190	0.001
12-12-80	Feed	7,794	5,144	84.4					
	Permeate	3,358	14	0.064					

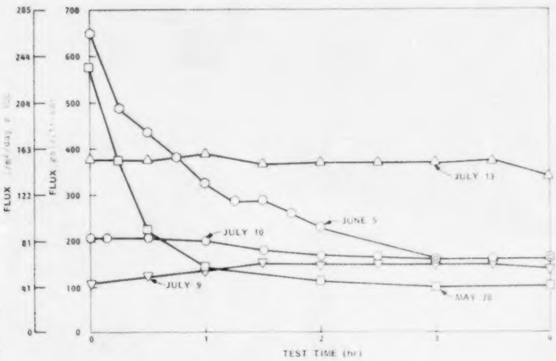

Fig. 3—Flux decline as a function of time.

precipitate a heavy metal such as cadmium.

During the eight-week evaluation, the plateau fluxes varied from the lowest value of less than 2040 l/m²/day (50 gal/ft²/day) to values over 16,300 l/m²/day (400 gal/ft²/day). The average flux varied between 6110 to 8150 l/m²/day (150-200 gal/ft²/day). This range was very similar to the results derived from the preliminary laboratory studies.

The permeate quality during the evaluation indicated, as shown in Table 1, that the microfiltration system was capable of removing suspended metals in the wastewater stream. Typically, in the effluent of the microfiltration system, cadmium was less than 0.5 ppm and suspended solids were less than 10 ppm when pH control was properly maintained.

Microfiltration System Application Study

The first full-scale HYDROPERM® microfiltration system was installed at the General Battery Company, Hamburg, Pennsylvania, in December, 1979. This system was a part of the total wastewater treatment system to remove suspended heavy metals from battery-manufacturing wastewaters.

The wastewater from lead-acid battery manufacturing is typically highly acidic with an approximate pH of 1 and contains a number of heavy metals including lead, antimony, arsenic, cadmium, nickel and copper. Some of these metals can appear in concentrations varying from 20 to 200 ppm. The wastewater lead-acid battery manufacturing characteristics can be considered to be similar to those of electroplating wastewaters with the exception of the absence of cyanides and hexavalent chrome. The conventional waste treatment technology for both industries is similar. Conventional neutralization/precipitation processes and solid/liquid separation processes are widely used.

Two MF units were designed, constructed, and installed at the General Battery plant with a combined wastewater treatment capacity of 188,000 lpd (50,000 gpd). Figure 3 gives a schematic of that system. Slaked lime was used in the neutralization tanks. No other chemical additives or flocculants were added. The systems have been operating since February 1980, and are maintaining an average flux rate of over 16,300 l/m²/day (400 gal/ft²/day). Currently, the permeate from the systems is of sufficient quality that it is being discharged to a public waterway without further treatment. Table 2 shows the tested permeate quality analyses from these systems.

CONCLUSION

Cross-flow microfiltration is an effective treatment technology to serve as unit process in the treatment train for industrial wastewaters containing heavy metals. The precipitated heavy metals formed by either caustic addition, as in the electroplating study, or lime addition, as in the battery study, can be easily separated from the wastewater if its pH is well controlled. Two full-scale microfiltration units installed at the Hamburg plant of General Battery have been successfully operating for two years. The quality of the treated wastewater is sufficient to permit discharge to public waterways or to local waterworks in the state of Pennsylvania. Although the electroplating evaluation program was conducted for only eight weeks, the results were similar to the results of the battery wastewater program. The resulting effluent is being discharged to the local public waterworks. Both evaluations indicate that microfiltration is a technology that can filter toxic heavy metal suspensions from industrial wastewaters.

ACKNOWLEDGMENT

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This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

The Application of Ion-Exchange and Modified Rinsing Procedures to Minimize Treatment Costs

Donald W. Kemp, Ph.D.*

INTRODUCTION

The capital cost of treating wastewater generated from a metal finishing operation is primarily a function of the rinse water volume to be treated. Many wastewater treatment systems installed during the 1970's were oversized since water conservation measures were not always fully exploited. It is anticipated that systems designed during the 1980's in response to the pretreatment regulations will be less costly due to the increased awareness of this factor.

However, the approach of minimizing water usage does not necessarily result in the lowest cost treatment system. It would be more cost-effective to focus on minimizing the quantity of process chemicals lost in the drag-out and to segregate residual drag-out loads into small rinse volumes that can be recovered or treated in a simple and inexpensive batch treatment system. By reducing pollutant loads discharged from the process line, operating costs as well as capital costs can be minimized. Background information on this approach is described below with an example of a system design to illustrate the application of in-line process controls.

DRAG-OUT CONTROL

The most effective pollution control measure is to keep the process chemicals in the process bath. This is most frequently accomplished by incorporating more effective drainage of drag-out from the work with longer drain times or modifying the position of the work. Methods to decrease the quantity of process chemicals lost in drag-out include reducing the chemical concentration in the process bath and installing exit sprays.

The actual reduction in drag-out losses that can be realized is strongly dependent on existing plant practices and the ability of plant management to initiate corrective action. It is not unreasonable to anticipate reductions in process chemical losses in the 25-50% range along with corresponding reductions in capital and operating costs. Because of these potential opportunities it would be prudent for plant management to initiate a process assessment to identify feasible alternatives that would be practical to implement. A more detailed description of point source controls has been recently published by EPA[1] which would provide background for this assessment.

DRAG-OUT SEGREGATION

The next line of defense to keep the process chemicals out of the rinse water is to segregate the drag-out in a still rinse or a slow rinse. The rinse concentrate can be returned to the process as evaporative make-up or batch treated. This approach requires the use of multiple rinse stations, however, space constraints can be a limiting factor. Off-line concentration of the drag-out can be accomplished by evaporation, electrolytic deposition, ion-exchange, or with membrane processes such as reverse osmosis and electrodialysis. These processes are relatively expensive and before they are seriously considered, a thorough evaluation of in-line process controls should be completed. Frequently, the addition of one or two rinse tanks in the process line can achieve similar results at far lower capital and operating costs.

The use of a drag-out recovery still rinse, followed by a fast rinse, is widely employed to recover process chemicals in the drag-out from a heated plating bath. It is less widely applied to control the contamination levels in the fast rinse to minimize the size and cost of a treatment system. A slow rinse can be used to remove the major fraction of the process chemical in a drag-out followed by a fast rinse to reduce the residual drag-out load to acceptable contamination levels for quality control purposes. If the residual load in the fast rinse is sufficiently low, it can be discharged without treatment since other non-contaminated rinses would provide a dilution factor. Alternatively, the lightly contaminated fast rinse can be economically treated by an ion-exchange process.

Generally a minimum of three and preferably four rinse tanks would be necessary to provide sufficient flexibility to adjust flow rates to achieve an acceptable degree of rinsing in the final or fast rinse and concentrate the pollutants in the slow rinse. Examples of alternative rinsing modes that could be considered under different process conditions are shown in Figure 1.

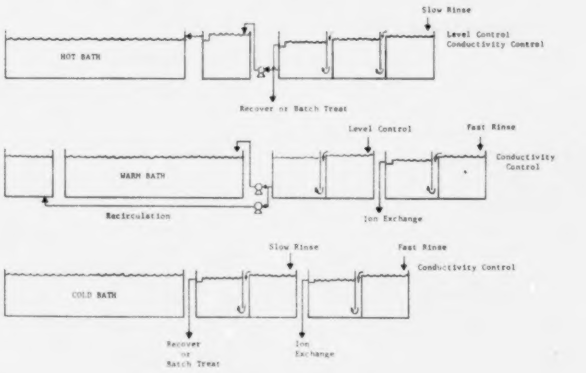

Fig. 1—Alternative Rinsing Modes.

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With a cold bath, the slow rinse concentrate can not be returned to the bath as evaporative make-up and would be discharged for batch treatment unless it was economical to consider an off-line process such as an electrolytic recovery unit. With a heated bath a closed loop rinsing system is shown where a sufficient degree of rinsing is achieved in the final rinse and all of the process chemicals are returned to the plating bath. Insufficient evaporation occurs with a warm bath to achieve high recovery by returning the slow rinse as evaporative make-up. In the example shown in Figure 1, a pre-dip in the rinse concentrate increases the recovery efficiency since process chemicals rather than rinse water are dragged into the plating bath.

To illustrate how drag-out losses can be reduced for a heated bath alternative rinsing modes are shown in Figure 2 for a heated Watts nickel bath. These baths are generally operated at 140-145° C with nickel salt concentrations in the 40-45 oz/gal range and typically have one drag-out recovery tank followed by one or two fast rinses. As shown in the first example, this would result in about one pound of nickel discharged into the final rinse assuming a drag-out loss of 1 gph over one shift.

The quantity of nickel discharged for treatment can be reduced by a factor of approximately 10 by decreasing the salt concentration and increasing the bath temperature by 10° F which almost doubles the evaporation rate. By operating the three rinse tanks as a 2-stage CF slow rinse followed by a single stage fast rinse 97% of the nickel can be recovered and 54 grams of nickel will be discharged compared to 520 grams in the first example. However, the nickel concentration in the final rinse is 14 mg/l versus 1.1 mg/l at the 2 gpm flow rate.

Another rinse tank can be added as shown in the third example to reduce the concentration. The evaporation rate could be doubled by increasing the bath heating time or by adding air agitation. The resulting 80 gpd flow in the 2-stage CF slow rinse would result in 99.8% nickel recovery and a residual nickel level of approximately 4 mg/l in a single stage 2 gpm rinse.

END-OF-PIPE TREATMENT

The driving force to control drag-out losses is to avoid the high cost of treating large volumes of lightly contaminated rinse water in a large treatment system that consumes valuable floor space in a non-productive activity. The capital cost for a conventional treatment system involving metal hydroxide precipitation is shown as a function of flow rate in Figure 3. These costs range from about $4000/gpm at the low flow rate, decreasing to about $2000/gpm at the high flow rate. Lower costs are associated with the batch reaction tanks that are made of plastic instead of coated steel.

Ion-exchange represents an end-of-pipe alternative to a conventional treatment process that can achieve a higher quality effluent. However, it has not been widely employed in the metal finishing industry because of higher overall costs that are associated with regenerating the spent resin.

A comparison of the capital costs curves shows that the ion-exchange treatment system is approximately one third the cost of a conventional treatment system. A relatively smaller cost would need to be added for a small bath treatment system to process ion-exchange regenerate, spent process solutions, floor spills, and other miscellaneous low volume, concentrated process discharges.

The higher operating costs for ion-exchange can be offset by taking a credit for the lower water usage by recycling the deionized water produced during treatment. With this credit, ion-exchange can be less costly than a metal precipitation process particularly in those cases where the cost of water includes a sewer use fee. A detailed cost evaluation and an in-depth description of the application of ion-exchange in the metal finishing industry has recently been published by EPA.[2]

ION-EXCHANGE POLISHING

The operating cost of ion-exchange can be significantly reduced if the system is operated as a polishing process rather than a primary treatment process. This can be accomplished by modifying the rinsing procedures in the process line to include the following:

1. Slow rinse - utilize a slow rinse to remove the majority of the ionic contaminant load in the drag-out; recover the rinse concentrate or treat the small volume in an inexpensive batch treatment system.
2. Fast Rinse - utilize a fast rinse to reduce the residual contaminant load in the drag-out to acceptable levels; process the lightly contaminated rinse water in an ion-exchange unit with periodic batch treatment of the regenerate.

This approach allows the major fraction of the hydraulic load to be treated with a lower capital cost compared to that by conventional treatment.

The operating cost is directly related to the regeneration

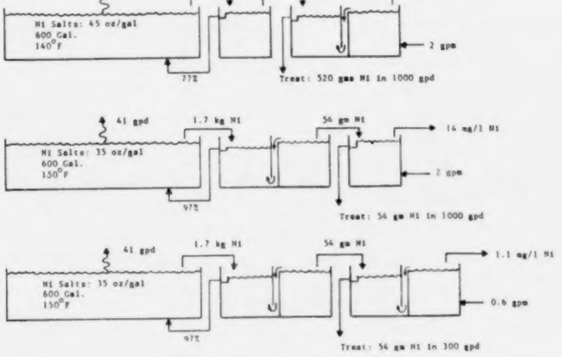

Fig. 2—Nickel Rinsing Alternatives.

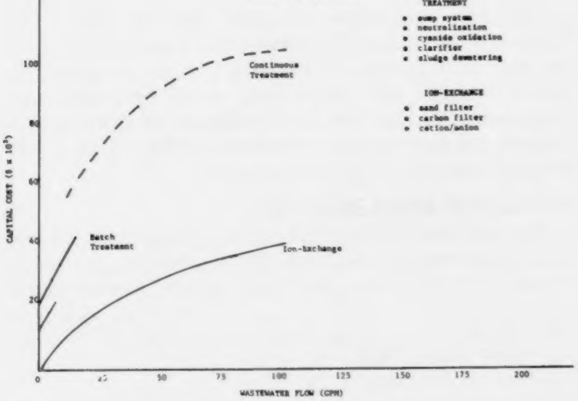

Fig. 3—Capital Cost Comparison.

frequency which in turn is a function of the flow rate set in the slow rinse. As shown by the curves in Figure 4 for a single and 2-stage CF chrome rinse, the regeneration frequency can be readily reduced by a factor of 10 or greater, along with corresponding reductions in operating costs.

In this example, one cubic foot of resin would saturate in approximately 2.5 hours if a 1 gph drag-out from a 40 oz/gal chrome plating bath were processed through the resin. (Resin capacity: 30 equivalents/ft^3). With a slow rinse set at 70 gpd, for example, the regeneration frequency would increase by a factor of 10 for a single stage rinse and a factor of 90 with a 2-stage CF slow rinse.

One objective in setting a slow rinse rate is to minimize the regeneration frequency and therefore the operational costs. A second objective is to minimize the volume of wastewater to be treated to minimize the capital costs. This volume consists of the slow volume and the ion-exchange regenerate. The latter includes the acid and caustic used to regenerate both the cation and anion columns and the slow and fast rinses. Typically about 10 column-volumes or about 150 gallons/ft^3 of contaminated wastewater are generated during cation and anion regeneration and require treatment. This volume can be reduced because not all of the fast rinse volume requires treatment. This, however, is offset somewhat by the need to periodically treat backwash water from the filter that precedes the ion-exchange column.

The average daily volume of regenerate per cubic foot of resin that would require treatment is shown as a function of the regeneration frequency in Figure 3. The point of intersection with the slow rinse curves represents the point where the total volume requiring treatment is minimized. For example, with a drag-out of 1 gph, a volume of 100 gpd or 50 gpd would require treatment depending on whether a single or 2-stage CF slow rinse is employed.

The data in Figure 3 illustrate that the operating cost of an ion-exchange process can be significantly reduced by using a slow rinse to reduce the ionic load discharged to the ion-exchange system. By coupling point source controls to minimize drag-out losses with ion-exchange treatment to

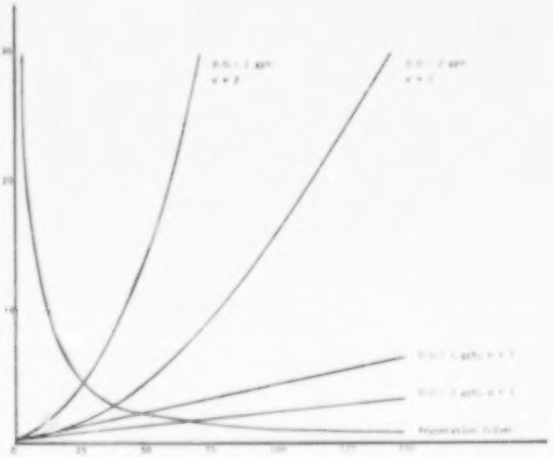

Fig. 4—Ion-exchange Regeneration Frequency as a Function of Slow Rinse Flow Rate.

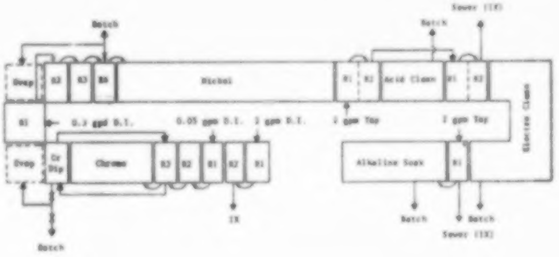
Batch
Sewer (IX)
Batch
Evap
R2
R3
R4
Nickel
R1
R2
Acid Clean
R1
R2
Electro Clean
R1
0.3 gpd D.I.
0.05 gpm D.I.
1 gpm D.I.
2 gpm Tap
2 gpm Tap
Evap
Cr Dip
Chrome
R3
R2
R1
R2
R1
Alkaline Soak
R1
IX
Batch
Batch
Sewer (IX)
Batch

Fig. 5—Automated Line.

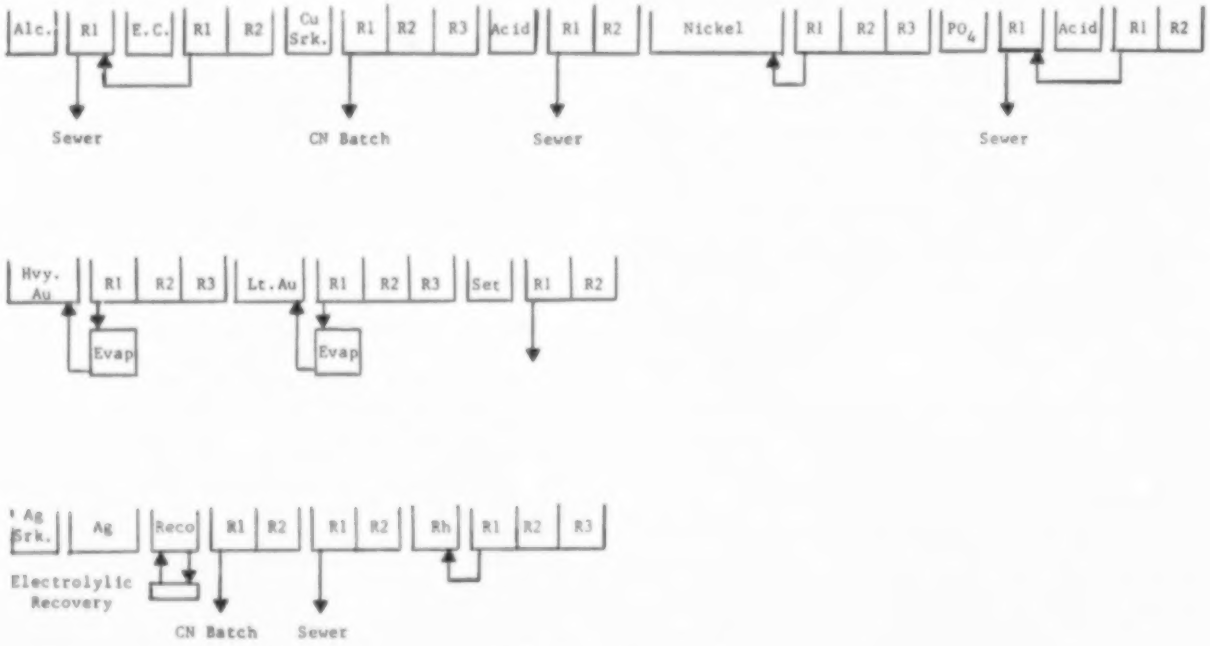
Alc.
R1
E.C.
R1
R2
Cu Srk.
R1
R2
R3
Acid
R1
R2
Nickel
R1
R2
R3
PO$_4$
R1
Acid
R1
R2
Sewer
CN Batch
Sewer
Sewer
Hvy. Au
R1
R2
R3
Lt. Au
R1
R2
R3
Set
R1
R2
Evap
Evap
Ag Srk.
Ag
Reco
R1
R2
R1
R2
Rh
R1
R2
R3
Electrolytic Recovery
CN Batch
Sewer

Fig. 6—Precious Metal Line.

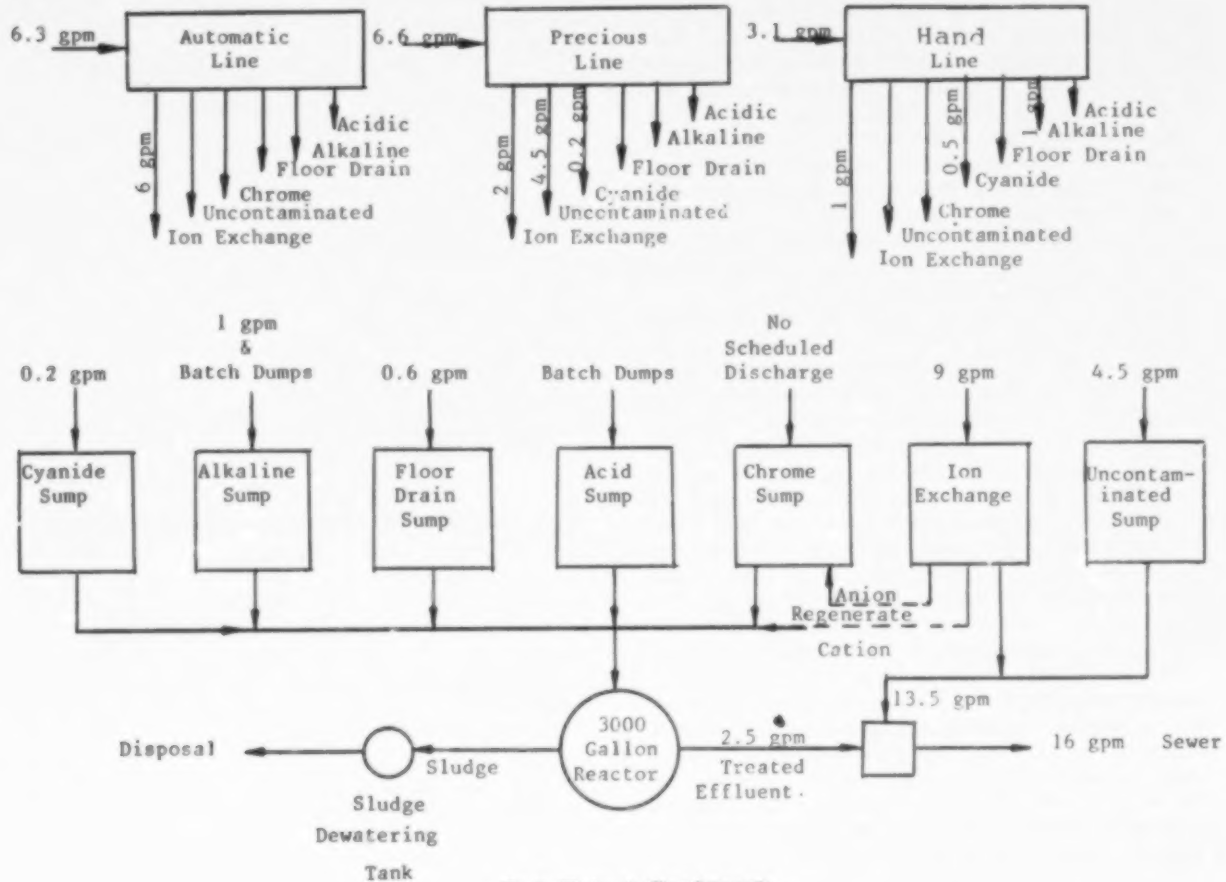
6.3 gpm
Automatic Line
6.6 gpm
Precious Line
3.1 gpm
Hand Line
6 gpm
Acidic
Alkaline
Floor Drain
Chrome
Uncontaminated
Ion Exchange
2 gpm
4.5 gpm
0.2 gpm
Acidic
Alkaline
Floor Drain
Cyanide
Uncontaminated
Ion Exchange
1 gpm
0.5 gpm
gpm
Acidic
Alkaline
Floor Drain
Cyanide
Chrome
Uncontaminated
Ion Exchange
0.2 gpm
1 gpm & Batch Dumps
0.6 gpm
Batch Dumps
No Scheduled Discharge
9 gpm
4.5 gpm
Cyanide Sump
Alkaline Sump
Floor Drain Sump
Acid Sump
Chrome Sump
Ion Exchange
Uncontam-inated Sump
Anion
Regenerate
Cation
13.5 gpm
Disposal
Sludge
Sludge Dewatering Tank
3000 Gallon Reactor
2.5 gpm
Treated Effluent
16 gpm
Sewer

Fig. 7—Wastewater Flow Schematic.

remove residual process chemicals in the rinse water, a cost-effective treatment system can be designed.

DESIGN OF A POINT SOURCE CONTROL SYSTEM

An example of how point source controls can be applied to minimize treatment costs has been demonstrated in one facility design for a plant that manufactures mechanical pens and pencils. The existing metal finishing operation incorporated an automated chrome line and a low volume hand line that included copper, brass, nickel, and chrome plating. The operation was to be moved to a new location and expanded to include a manual precious metal line. The company required a wastewater treatment system to be designed to satisfy the sewer use ordinance which included the following limits (mg/l): CN - 0.5; Cu - 1.0; Ni - 3.0; Cr - 3.0; Ag - 0.03).

A systematic evaluation of each process bath was conducted to define process specifications that would minimize treatment costs and process chemical losses. The approach focused on reducing drag-out losses and the use of counterflow rinsing to minimize the volume of wastewater requiring treatment.

Automated Line

The automated chrome line involves rack plating of a variety of brass components that include tubular pieces. Drag-out rates in the existing line were measured to be 1 - 1.5 gph. It was determined that the majority of the drag-out could be more effectively drained by tilting the rack and a redesigned rack will be used for rack replacements

The layout of the new automated line is shown in Figure 4 and consists of a single stage rinse after the alkaline soak and a 2-stage CF rinse after the acid cleaning bath with the discharge used as the supply for the 2-stage CF rinse after the electroclean bath. The soluble copper concentration in the cleaning bath was found to approach 150 mg/l near the end of the 2-3 week cleaning cycle. It was calculated that this would result in a copper concentration in the combined discharge in excess of the 1 mg/l limit toward the end of the cleaning cycle. To offset this factor, exit sprays were specified in each of the three cleaning baths which would enable the rinse water to be discharged to the sewer without treatment. As a precaution the discharge could be directed to an ion-exchange unit which was sized to process the rinse water from all the cleaning baths in the automated and manual lines.

Four CF rinses were used after the 1800 gallon nickel bath (heated at 150° F) to close the rinsing loop and recover 100% of the nickel salts. The standby capacity in the off-line evaporation tank and facilities for air agitation in the nickel tank would enable the slow rinse to be increased if required. All of the slow rinse concentrate is returned to the bath as evaporative make-up via the exit spray by pumping from R4. A conductivity flow control in R1 would enable additional water to be added if necessary and any excess rinse water that could not be returned as evaporative make-up would be pumped to the evaporation tank or discharged to batch treatment.

The chrome rinsing sequence consists of a 3-stage CF slow rinse (0.05 gpm) with recirculation from R3 to a chrome pre-dip tank. A stand-by tank provides additional holding capacity to evaporate any excess slow rinse that can not be returned to the chrome bath via an exit spray pumped from R3. Over 95% recovery is expected. The 2-stage CF final rinse would remove the residual chrome in the drag-out to achieve a final calculated chrome concentration of 1 mg/l. The final rinse would be discharged to an ion-exchange unit to remove the residual chrome which is estimated to be less than 250 gms/day.

Precious Metal Line

The precious metal line involves manual rack plating of gold, silver, and rhodium. The rinsing system in this line was directed at achieving the following objectives:

1. close loop rinsing after the nickel bath
2. recovery of greater than 99% of the gold and rhodium
3. segregation of greater than 90% of the cyanide load from the copper strike and silver baths into a slow rinse
4. reduction of water usage by inter-loop rinsing where feasible.

A drag-out rate of 0.5 gph was assumed in the calculations to determine concentrations, flow rates, and optimum arrangement of rinsing tanks.

In the cleaning line it was established that a 3-stage CF rinse after the copper strike and nickel baths would be adequate to satifsy the rinsing objectives. A conductivity flow control would be used to ensure that acceptable concentration levels would be maintained in R3. With a slow rinse flow rate set 25 gpd to match the evaporation rate in the nickel bath essentiallly 100% of the nickel salts would be recovered. Back-up evaporation capacity in the 150° F nickel bath is available through air agitation if an increase in the slow rinse flow is required.

In the gold line an off-line air agitated evaporation tank was used to further concentrate the slow rinse from the 3-stage CF rinse after the heavy and light gold baths. By returning the concentrate to the heated gold baths (110-120° F) as evaporative make-up, 99% of the gold could be recovered. This approach eliminated the need to use an off-line gold recovery process. If it is established that gold leakage from inefficient rinsing occurs, it would accumulate in the set rinse and an ion-exchange unit would be installed to recover the residual gold.

The rinsing sequence after silver plating consists of an electrolytic recovery rinse followed by a 2-stage CF slow and fast rinse. The slow rinse flow of approximately 25 gpd was calculated to segregate over 99% of the cyanide load. The residual cyanide load in the fast rinse would result in an acceptable effluent concentration after dilution with the other rinse water.

A 3-stage CF closed loop rinse was employed after the rhodium bath to recover over 99% of the rhodium by returning the slow rinse to the bath as evaporative make-up. The evaporation rate is maximized by employing air agitation in the bath at elevated temperatures during periods of non-plating activity.

WASTEWATER TREATMENT SYSTEM

As shown in the wastewater flow scheme in Figure 7, 16 gpm of wastewater is expected to be generated from the three process areas. The only sources that require treatment are:

- 2 gpm of lightly contaminated chrome rinse water
- approximately 100 gpd of cyanide contaminated rinse water

The remaining wastewater can be discharged to the sewer without treatment as the residual contamination levels would be below the EPA limits promulgated in the Electroplating Pretreatment Regulations and the more stringent local sewer use limits.

The 100 gpd of cyanide contaminated rinse water would be discharged to a 600 gallon reaction sump and batch treated on a weekly basis. The contaminated chrome rinse water would be processed in an ion-exchange unit which has an anion resin capacity (4 ft^3). This would enable the unit to be operated for over four weeks before regeneration would be required. The regenerate would be batch treated in a 500 gallon reaction sump to reduce the hexavalent chrome to chrome III.

The ion-exchange system which costs approximately $16,000 is a skid mounted semi-automatic unit that consists of a sand filter, a carbon column, and a cation and anion column each containing 4 ft^3 of resin. The system which has a hydraulic capacity of 8-12 gpm was sized to process rinses from the cleaning, chrome, and silver baths. Initially the deionized water (DI) produced in the system will be discharged to the sewer and the installation of a DI water recirculation system will be delayed until after the metal finishing operation is brought on-line in the new facility. Plant management elected to install a second back-up ion-exchange system which will be used initially to provide DI water for the metal finishing operation using town water rather than wastewater as the supply source.

The remaining wastewater sources include:

• schedule batch dumps (normalized over cleaning cycle):	300 gpd
• vibrator discharge (design specification):	500 gpd
• floor spills (estimated):	300 gpd
Total	1100 gpd

These discharges would be directed to the acid, alkaline, and floor drain sumps and pumped to a 3000 gallon batch reaction tank to neutralize the combined discharge and remove metallic fines and soluble metal.

SUMMARY & CONCLUSIONS

The facility design described above illustrates that in-process controls can be integrated into a process line to maximize recovery of process chemicals and significantly reduce treatment costs. The success of this approach is highly dependent on plant management initiating a detailed process evaluation to identify procedures to minimize drag-out losses and to locate sufficient space in the process line to incorporate additional rinsing. This approach would enable ion-exchange to be considered as an economical alternative to conventional treatment involving metal hydroxide precipitation.

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The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

Recovery of Acid Etchants at Imperial Clevite Inc.

William J. Herdrich*

ABSTRACT

Imperial Clevite recovers two etching solutions at its plant in Niles, IL, a chromic acid-sulfuric acid etching solution and a nitric acid solution. The chromic acid-sulfuric acid etching solution is regenerated and recycled through a unit developed by the U.S. Bureau of Mines. The nitric acid solution is recycled through a unit made by Eco-Tec Ltd. of Canada.

The Bureau of Mines unit has regenerated and recycled etching solution from a chromating operation for brass parts during normal production for six months. The etching solution has been maintained at an acceptable level of performance, and consumption of sodium dichromate has been reduced by 70%. Waste generation has been reduced by 76%, and the cost of the operation has been reduced 73%.

The Eco-Tec unit has only been in operation for a few days as of this date. Results, so far, look positive.

INTRODUCTION

Imperial Clevite Inc. is a multi-divisional company whose operating divisions are based upon similarity of products. The Fluid Components Division is one such division. The Fluid Components Division produces products relating to connection and control in fluid power systems. The division's valves, fittings, testing devices and tubing tools are used in process instrumentation control, truck air brake components, refrigeration evacuation, pneumatic and other air devices.

In the production of these products the Fluid Components Division operates a plating and metal finishing operation. This operation produces wastes which must be controlled. In 1980 while designing and installing a system to control these wastes, means of recovering and recycling chemicals and metals were investigated. As a result of these investigations it was determined that the "bright dipping" operation, a chemical surface treatment used to give brass parts an attractive appearance and provide corrosion resistance, produced the most chemical and metal waste and that it might be possible to recover some of this waste.

"BRIGHT DIPPING" OPERATION

The "Bright Dipping" Operation is used to give brass parts an attractive appearance and provide corrosion resistance. This is very important for forged brass parts to remove the scale and oxides present after forging. The process consists of muriatic acid etching to remove scale and oxides, nitric acid etching to provide a very smooth, bright finish, and a chromic acid-sulfuric acid etching to provide a lustrous finish while applying a corrosion resistant coating. A noticeably less attractive finish indicates failure of one or more of the etching solutions. Failure of the etchants results from an increase in the concentration of dissolved metals or a decrease in the free-acid content of the solution. The chromic acid-sulfuric acid etchant is also quite sensitive to increases in chloride contamination, which is caused by drag-in of the muriatic acid etchant. Failure of the chromic acid-sulfuric acid etchant is very noticeable as a dull, mottled finish on the part with a slightly red coloration, which gives an extremely unattractive appearance. Usually failure of the etchant solutions can be delayed by simple additions, but the working life of the solutions cannot be significantly lengthened. When the etchant solutions degrade beyond the point of rejuvenation by chemical addition, they are chemically treated by standard methods to produce a low-grade sludge containing 1 to 10 percent solids.

Of the three etchants used in the bright dipping operation only two, the chromic acid-sulfuric acid etchant and the nitric acid etchant were chosen for recovery based on cost.

Recycling of Chromic Acid-Sulfuric Acid Etchant

The recycling of chromium is not new. The Bureau of Mines has been engaged in research on the subject for some time, and it happened that in 1980 they had developed a test unit for the recycling of chromic acid-sulfuric acid solutions and were looking for a test site. Imperial Clevite's Fluid Components Division, then the Fluid Components Division of Gould Inc., volunteered to be the test site since the Bureau of Mines test unit had a direct application to its operation.

The unit designed by the Bureau of Mines was an electrolytic acid recovery system. The technology for the unit was described at this conference last year by representatives of the Bureau of Mines.[1] Basically, the unit oxidizes trivalent chromium to hexavalent chromium and simultaneously recovers copper and zinc. The unit uses anode membrane cells in a catholyte tank. The copper is recovered as a solid and the zinc remains in the catholyte solution.

The test was conducted from May 31 to June 16, 1980. Calculated results from the test showed that 40.9 percent of the Cu contamination was removed, 21.1 percent of the Zn contamination was removed, and 81.2 percent of the trivalent Cr was converted to hexavalent Cr. Table I shows

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Table I
Chemical Analysis of Chromic Acid-Sulfuric Acid (CSA) Etching Solution Before, During, and After the Bureau of Mines Unit Operation[2]

	Cr^{6+} (pct)	Cu (g/l)	Zn (g/l)	Cl (ppm)
Spent CSA etchant	86.5	8.0	3.7	320
CSA etchant during operation (average)	94.0	3.2	2.0	64
CSA etchant at end of operation	99.3	1.3	2.0	5

analysis of the etchant samples during the test.[2]

The optimum conditions for chromic acid-sulfuric acid etchant are: pH of 0.8 to 1.2 and 8 oz/gal $Na_2Cr_2O_7 \cdot 2H_2O$.* Prior to the use of the Bureau of Mines test unit preparation of the etchant required 50 lbs of $Na_2Cr_2O_7 \cdot 2H_2O$. Periodic additions were made to maintain optimum operating conditions. After approximately two days and approximately 36 lbs of additions, the etchant became ineffective and was treated and discarded. Therefore, the average weekly consumption of $Na_2Cr_2O_7 \cdot 2H_2O$ was 215 lbs. Treatment and disposal of the etchant generated approximately 1,750 gal/wk of low grade sludge.

During the Bureau of Mines test the weekly $Na_2Cr_2O_7 \cdot 2H_2O$ consumption was 56 lbs. The waste produced by the unit created approximately 125 gal of sludge per week. This was a drastic reduction from the 215 lbs/wk of $Na_2Cr_2O_7 \cdot 2H_2O$ and 1,750 gal/wk of sludge produced during normal operation.

Based on the results of the Bureau of Mines tests, Imperial Clevite contracted for Scientific Control Laboratories to produce an industrial model of the Bureau of Mines test unit. This unit was completed in January of 1981 and in operation by March of 1981. Except for some minor problems causing shutdowns for short periods of time, the unit has been running consistently since March 1981. Since installation of the unit, consumption of $Na_2Cr_2O_7 \cdot 2H_2O$ has been approximately 50 lbs/wk. Sludge produced has been approximately 200 gal/wk.

The major costs of operating the chromic acid-sulfuric acid etching solution are $Na_2Cr_2O_7 \cdot 2H_2O$ consumption and sludge haulage. The market price for $Na_2Cr_2O_7 \cdot 2H_2O$ is approximately $.68/lb. Prior to installation of the recovery unit the operation consumed 215 lbs/wk costing $145/wk. Sludge haulage charges for the Niles area are approximately $.20/gal. Cost of hauling the 1,750 gal/wk produced prior to installation of the unit was $350. The total of these major costs for operating a chromic acid-sulfuric acid solution prior to installation of the recovery unit is $495/wk. Since installation of the Scientific Control Unit, $Na_2Cr_2O_7 \cdot 2H_2O$ consumption has been averaging 50 lbs/wk at a cost of $34/wk. The unit produces approximately 200 gal/wk of waste to be hauled costing $40/wk. Based on these figures the cost of operating the chromic acid-sulfuric acid solution with the recovery unit is approximately $74/wk. Also the copper is recovered in a solid form. In the first four months of operation, 500 lbs of 98% pure copper were extracted from the unit.

The recycling unit for chromic acid-sulfuric acid solution has been effective at maintaining the etchant at an acceptable performance level and reducing the consumption of $Na_2Cr_2O_7 \cdot 2H_2O$. The reduction of $Na_2Cr_2O_7 \cdot 2H_2O$ and sludge generation resulted in significant cost reductions. The cost of $Na_2Cr_2O_7 \cdot 2H_2O$ usage and sludge haulage prior to installation amounted to $495/wk. After installation, the cumulative costs of $Na_2Cr_2O_7 \cdot 2H_2O$ consumption and sludge haulage amounted to $74/wk, resulting in a $421 per week reduction in normal operational costs for these items.

Recycling of Nitric Acid Etching Solution

The recycling of nitric acid is done by an Acid Purification Unit marketed by Eco-Tec Limited, Toronto, Canada. The unit is designed to continuously maintain bath integrity by removing metallic contaminations as they are generated. As a result:

1. Acid purchases are reduced
2. Waste treatment costs are reduced
3. Process operation is stabilized

The Acid Purification Unit uses an ion-exchange resin bed and recirculating flow to recycle the nitric acid. The resin bed absorbs mineral acids leaving a de-acidified metallic salt byproduct which is treated and disposed of. The acid is removed from the resin bed by forcing water through the resin with air pressure. The result is a purified acid which is returned to the etching tank.[3]

Operation of the nitric acid etching solution without the Acid Purification Unit consumed approximately 400 gal/wk of nitric acid and produced 3,500 gal/wk of waste. The market price for nitric acid is approximately $1.43/gal. For a consumption of 400 gal/wk the direct cost is $572/wk. Sludge hauling charges for the Niles area are approximately $.20/gal. Cost of hauling 3,500 gal/wk is $700/wk. The total cost then for operating the nitric acid etching solution is $1,272/wk. Since installation of the Acid Recovery Unit, nitric acid consumption has been approximately 200 gal/wk. With the unit operating, the operation still produces 3,000 gal/wk of waste, eliminating only 500 gal/wk. Based on these figures the cost of operating the nitric acid bath with the Acid Recovery Unit is $868/wk, a savings of $386/wk.

CONCLUSION

The recycling of the acid etchants at Imperial Clevite has been successful. The consumption of both nitric acid and $Na_2Cr_2O_7 \cdot 2H_2O$ have been reduced significantly. The cost of waste hauling has been reduced, and the etching operations run more consistently.

To a manufacturing organization the most important aspect is the cost reduction. The cost savings for these two operations will be approximately $40,000/yr.

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The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

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*$Na_2Cr_2O_7 \cdot 2H_2O$ is the chemical representation for sodium dichromate.

Recovery and Electrochemical Technology

Philip Horelick*

INTRODUCTION

I shall discuss the experience of a job shop with the **installation of an High Surface Area (HSA) electrochemical Reactor and associated in-plant changes. The Reactor** has been installed to recover cadmium and destroy cyanide on two plating lines.

My paper focuses on the practical aspects of the technology, such as operating performance and cost savings, and discusses process water and pollutant reduction techniques that were instituted before the HSA Reactor was installed.

ALLIED METAL FINISHING—BACKGROUND

Allied Metal Finishing, Inc., is a metal finishing job shop that has operated in Baltimore, Maryland, since 1947. Our 35,000-square-foot plant employs 50 people working three shifts a day. Sales are more than $1.5 million a year.

Our plant is a multipurpose shop with the following major facilities:

- Automated powder coating line
- Fluid-bed tank
- Barrel line
- Anodizing line
- Hoist line
- Automated zinc line
- Hard chrome line
- Electroless nickel line
- Precious metals line
- Chemical mixing

Zinc and nickel plating account for the major part of our company's total volume. Cadmium plating currently accounts for 10 percent of the total volume and is expected to increase.

Before the installation of the electrochemical technology and the implementation of waste reduction techniques, our effluent discharge was approximately 100,000 gal/d. The City of Baltimore, Department of Public Works, initiated a monitoring program in 1975 to measure the pollutant concentration of electroplaters and other industrial contributors to the city waste treatment system. The monitoring indicated that the Allied effluent would require some treatment in order to meet upcoming Federal standards.

Although the deadline for electroplating wastewater pretreatment was some time away, we decided to initiate compliance efforts in 1979. The additional time would allow for an analysis of various treatment alternatives and would eliminate a last-minute rush to purchase and install equipment.

We approached the Baltimore Department of Public Works to determine what parameters were of most concern. The Department responded that cadmium was its biggest problem, because high levels of the toxic element in the sewage treatment sludge can reduce the City's disposal alternatives.

The City's records (Table 1) indicated that Allied had a maximum cadmium discharge of 1.50 mg/L. The 4-day average ranged between 0.45 mg/L and 0.82 mg/L. The 1984 Federal pretreatment standards for cadmium allow a maximum of 1.2 mg/L for any one day and 0.7 mg/L for 4 consecutive monitoring days. Therefore, we were on the borderline of compliance.

We expected, however, to increase cadmium production significantly in the future, which would invariably push the cadmium concentration well beyond the Federal limit. We had projected the increase in cadmium plating because many platers around the United States have reduced or eliminated their volume of cadmium plating owing to local attitudes similar to that of the City of Baltimore. Thus there is incentive to find a cadmium control technology because, with fewer cadmium platers in existence, such a technology may be a beneficial tool for future business. Therefore, our efforts were initially focused on cadmium.

POLLUTION CONTROL PROJECT

Conferences and exhibits of the American Electroplaters' Society (AES) and the National Association of Metal Finishers (NAMF) provided a mechanism to view the various pollution control devices available to the plating industry. At a 1979 NAMF show in Chicago, we were introduced to the HSA Reactor, an electrochemical technology designed for the recovery of various metals, including cadmium.

We were attracted to the HSA technology for two major reasons. First, the electrochemical technology removes cadmium without the use of treatment chemicals and without creating a sludge, thus avoiding sludge transportation and disposal costs, which most pollution control experts agree are the major operating expenses for pollution control systems. Second, in the approach developed by HSA personnel, the HSA technology is used as part of a general compliance strategy that includes making manufacturing process changes to reduce water use and pollutant loadings. End-of-pipe treatment is only applied after less costly in-plant changes and point source recovery techniques, such as the HSA Reactor, are implemented.

After meeting with personnel from HSA and discussing the advantages of the approach, we decided to use the HSA compliance strategy and Reactor.

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Table 1
Allied Effluent Analysis

Date	Cd	Al	Cu	Zn	Ni	Fe	Cr(T)	CN	Pb	pH	Daily Flow[1] (1,000 gal)
	Concentration (mg/L)										
2/3/75	1.50	5.0	1.05	17.0	2.3	37.0	—	—	—	6.82	116
8/26/75	1.11	3.8	1.26	6.8	0.95	—	—	—	—	8.65	116
9/18/75	—	—	—	—	—	—	2.49	2.32	—	7.8	116
6/10/76	0.40	3.0	1.15	3.5	0.05	14.0	7.5	0.23	—	5.46	155
3/17/78	0.27	—	0.52	4.8	4.85	—	7.33	1.48	0.19	8.05	98
5/26/78	0.16	—	1.05	—	105.0	—	2.91	—	—	6.50	98
6/8/78	0.44	—	0.39	8.20	0.48	—	2.82	—	—	9.41	98
11/9/78	—	—	—	—	—	—	—	—	—	9.10	98
6/22/79	—	—	—	—	—	—	—	—	—	8.07	127
3/18/80	0.92	8.9	0.36	3.9	0.90	—	—	—	—	2.82	66
11/17/80	—	—	—	—	—	—	—	—	—	2.28	66
3/23/81	0.43	1.14	1.28	12.38	2.46	—		—	—	6.04	†
6/17/81	—	—	—	—	—	—	-	-	—	7.77	†
10/6/81	0.28	—	0.90	11.0	3.26	—	5.0	11.6	0.46	—	†
12/1/81	0.22	—	—	15.5	3.05	—	4.29	7.54	—	—	†

[1] Average daily flow for year indicated.
†Data for 1981 not yet available.
Note.—Dash indicates not reported by the city.
SOURCE: City of Baltimore, Department of Public Works, Bureau of Water and Waste Water.

PLANT ASSESSMENT

The compliance strategy was initiated with a plant assessment survey, which involved a thorough analysis of the plating operations that relate to pollutant sources and water use. The procedures used by the survey team included:

- Reviewing plant layout, including equipment placement piping, and sewer line layout
- Reviewing plant operating practices and procedures
- Conducting a process water survey
- Sampling to determine the type, quantity, and nature of pollutants
- Isolating and identifying the sources of pollutants
- Examining process water use

The findings of the survey were presented in a 75-page report that provided a detailed breakdown of water use in the shop, a chemical balance, and, most important, 46 specific recommendations for saving water and chemicals and reducing pollution.

Some of the recommendations related to operating practice such as instructing operators to turn off the main water valve during breaks and other line stoppages. Others involved the application of inexpensive devices to reduce water flow automatically. For example, one effective recommendation for Allied was to install timer devices on two of the plating lines for the control of water flow. This action was deemed appropriate because the amount of time between loadings through the rinse tanks was significantly long that with a constant flow most of the rinse water used was wasted. The timer reduced water use on these lines by over 65 percent.

Most of HSA's 46 recommendations have been instituted. Others are planned or will be considered when individual plating lines are overhauled. The results thus far are very positive. Overall, we were able to reduce the rate of water use by 52 percent. Savings in water and sewer costs alone are about $7,000 per year as indicated in Table 2, which presents a history of water use at Allied from 1974 through 1980. The HSA recommendations were instituted in January 1980. That year our water use rate dropped from 127,000 gal/d to 66,000 gal/d. It is even more significant that sales remained about the same during that time period. A comparison of flow rate and sales are presented in Figure 1.

Chemical use has also dropped since the HSA recommendations were instituted.This decrease is a result of using drag-out tanks to capture plating solution and return it to the baths.

HSA REACTOR

After implementation of the in-plant changes for flow and pollution reduction, the HSA Reactor was installed.

The Reactor is an electrochemical technology and, therefore, its operating principles are easily understood by the average plater. The unit makes use of a carbon fiber cathode, which has an enormous surface area to volume ratio—approximately 1,000 times greater than that of other types of reactors. This high surface area provides a greatly improved mass transfer rate. The result is that the time required to reduce the concentration of a metal in solution is a small fraction of that, for instance, for catalytic or fluidized bed reactors.

Table 2
History of Water Use: 1974 to Present

Year	Consumption gal/d	Consumption gal/min	Cost $/1,000 gal	Cost $/Year
1974	228,000	158	0.34	20,504
1975	116,227	121	0.37	11,130
1976	155,724	108	0.40	16,574
1977	125,998	87	0.46	14,944
1978	97,888	68	0.52	13,356
1979	127,186	88	0.52	17,227
1980	65,777	46	0.58	9,928

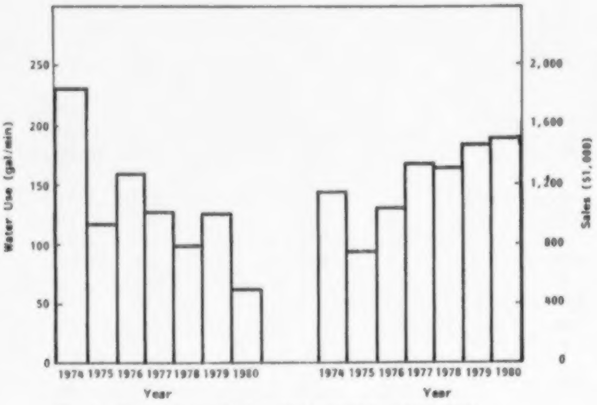

Fig. 1—Comparison of Water Use and Sales: 1974-1980.

In addition to recovering metal and returning it to the plating bath for reuse, the Reactor can electro-oxidize and destroy cyanides below detection limits at a cost much lower than the conventional alkali-chlorination process.

The Reactor originally installed at Allied was a prototype unit. After HSA had fully developed the technology, the current commercial unit replaced the prototype.

Initially the Reactor was used to recover cadmium from the barrel line only. Recent piping changes have been made, however, and the Reactor now services the hoist line as well.

The Reactor itself is a skid-mounted unit needing approximately 20 square feet of floor space. The space requirement includes the microprocessor control, which regulates solution flow during the process cycle and automatically reverses the system to a strip cycle for metal recovery.

Figure 2 shows the HSA Recovery System in a single line arrangement. The solution from the process rinse is pumped through a filter to remove particulate matter, and through the Reactor modules, which house the high-surface-area carbon fiber cathode. The treated water is returned to the process tank. The power for the treatment process is supplied by a common rectifier.

When the hoist line was added to the system (Figure 3), the flow from the Reactor went first to the hoist line process tank, then was pumped to the barrel line process tank and back to the Reactor for cadmium removal and cyanide destruction.

Although the HSA Reactor is capable of recovering in excess of 99.9 percent metal pollutants, it is not necessary to achieve such high levels at our plant in order to meet existing environmental regulations. Current needs call for a system equipped with only two modules; however, the unit is capable of housing up to four modules, thus providing an easy means to meet future higher capacity requirements.

The operation of the Reactor system is fairly simple and not time consuming. Our unit is operated by the company chemist, Julius Schattall. When the cadmium plating line is used, Julius starts the Reactor by pushing a button, which initiates the process cycle, and the solution from the process rinse is pumped through the modules for cadmium removal and cyanide oxidation. When plating is completed, pushing a second button stops the process cycle and initiates the strip cycle. When stripping is completed, the unit shuts down automatically.

The strip solution is made up using sodium cyanide. The concentration of cyanide in the solution is monitored periodically and is kept in a range of 50 to 100 g/L. The volume of the strip tank is about 135 gallons.

The strip solution remains in the strip tank for several operating cycles, gradually increasing in cadmium concentration. The maximum allowable concentration is 60 g/L. When the solution level in the plating bath is sufficiently low, a part or all of the strip solution is pumped to the bath to complete the recovery process. The strip solution is not pumped to the plating bath on a set schedule, but usually twice a month.

COST SAVINGS

The institution of water reduction techniques resulted in a cost savings of $7,000 the first year. The savings will undoubtedly be more signigicant in 1981 because of a 26 percent increase in Baltimore water and sewer rates. In addition to these savings, our cadmium use has decreased. Before the HSA Reactor was installed, we consistently had

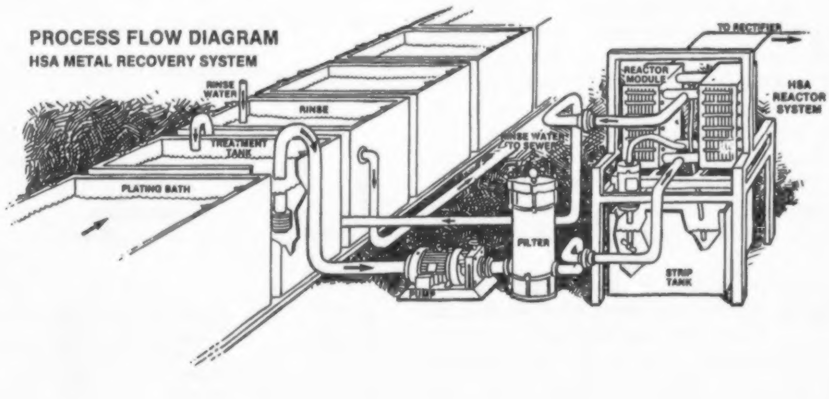

Figure 2.

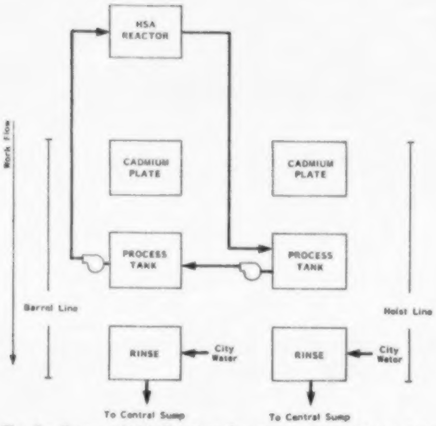

Fig. 3—Current HSA Reactor System at Allied Metal Finishing.

a cadmium-use-to-sales ratio of 0.13. Since the Reactor was installed, the ratio has dropped to 0.09—a 31 percent reduction in cadmium purchases.

By reducing treatment chemical needs and sludge production, the Reactor will be saving even more money when the Federal pretreatment regulations are enforced. Sludge disposal is a major concern for us at Allied, because we are currently paying $1.35 per gallon for disposal of RCRA-manifested waste. At projected production rates, these savings will be over $10,000 per year.

SYSTEM MONIRTORING

As I discussed earlier, the Baltimore Department of Public Works has monitored industrial effluents since 1975. When the Reactor was installed, the Depatment was invited to evaluate the effectiveness of the technology in reducing the cadmium concentration of the effluent. The Department agreed, and set up monitoring equipment in March of 1981. The results were phenomenal—the cadmium concentration in the effluent was 0.432 mg/L. Most remarkably, this concentration was achieved at the new low flow rate and during a period of high cadmium plating production.

The Department of Public Works was impressed with the results. Since March, the Department has monitored on two other occasions. The results were 0.28 mg/L and 0.22 mg/L cadmium. The numbers were so low that the Department began reporting the concentrations on its official forms in parts per billion rather than in the conventional parts per million or milligrams per liter.

CONCLUSIONS

The results to date indicate that our decision to use HSA was excellent. The primary goal of finding a cadmium control technology to meet current and future demands has been met. We are now in a position to increase our cadmium plating volume without environmental worries at a time when many platers are leaving the market. In addition, we expect substantial cost savings once the Federal pretreatment standards have been implemented.

The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

Some Successful Applications of Electrodialysis

William G. Millmam and Richard J. Heller[*]

Metal recovery from plating solution dragout has become a prime concern for many metal finishers lately. To satisfy the demand for metal recovery, many new recovery systems have been introduced into the market. Electrodialysis (ED) has been one of the more successful systems introduced over the past five years. Some of the most successful applications will be reviewed in this paper.

In order to fully understand the application of electrodialysis, a brief discussion of the theory follows.

Electrodialysis, in the pure sense, is the movement of ions through ion selective membranes, under the influence of an electromotive force (voltage) applied across the membrane area. Ion exchange membranes are the key to this process and exist in two basic distinct forms—cationic and anionic.

Cationic membranes allow only the positively charged ions such as copper, zinc or nickel to pass through them, while conversely, anionic membranes allow only the passage of negatively charged ions such as chloride and sulfate, or cyanide complexes, etc. These membranes are thin sheets of plastic material which have been subsequently impregnated to impart the appropriate ionic characteristic. Membranes then when arranged in parallel cells between two electrodes, positive and negative, along with specifically designed spacers and gaskets to separate the membranes into leak-tight cells, give the basic construction of an electrodialysis stack.

Figure 1 is a schematic operational drawing of such an ED stack. At each end are the electrodes, a cathode of stainless steel and an anode of platinum-clad titanium. Each electrode is in a cell around which flows a compatible salt solution of electrolyte whose purpose is to collect and dispel resultant gases such as hydrogen and oxygen and impart overall electrical conductivity to the stack. Subsequently, there are a number of individual cell compartments of alternating layers of anionic and cationic membranes. The even numbered cells are the paths for the feed solution; the feed solution being the constantly circulated solution from a dragout or reclaim tank. The odd numbered cells are the collecting, or concentrating, cells in which the concentrated plating solution is collected for return to the plating tank. The cations are the metal ions such as nickel, copper, zinc, etc. which are attracted to the left toward the cathode, but can only move into the next adjacent cell where they are prohibited from further migration by an anionic membrane. Likewise, the anions such as the chloride, sulfate, etc. are attracted to the right side, but again are prohibited from further migration by the presence of a cationic membrane. Since the entire system must be electrically neutral, the recovered or concentrated solution is collected in the odd numbered cells while the reclaim rinse solution, that is circulated in the even numbered cells, is constantly being reduced in metal salt concentration.

Figure 2 shows this process in schematic fashion. This ongoing process then is engineered in terms of stack size to remove the same volume of plating solution as is dragged out of the plating tank into the reclaim tank during the normal production operation. The remaining components in an operational electrodialysis unit consist of a rectifier to provide the appropriate potential across the two electrodes, a pump to circulate the electrode rinse, and a pump and filter to circulate the reclaim rinse through the ED stack. This then, along with the appropriate monitoring system and meters, constitutes an operational electrodialysis unit as can be seen in Figure 3.

ED Application in Gold Plating Operations

Circuit-wise

Some of the most successful applications of ED have been on gold plating baths. The high conductivity of typical

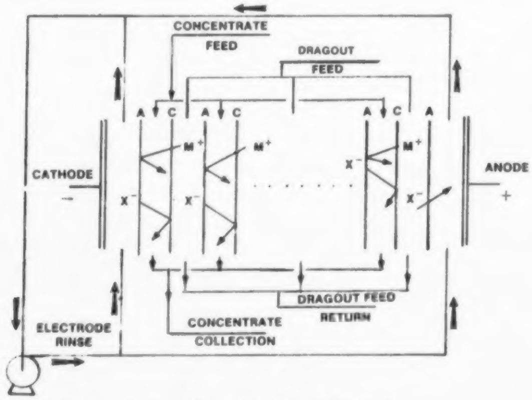

Fig. 1—Schematic Operational Drawing of ED Stack

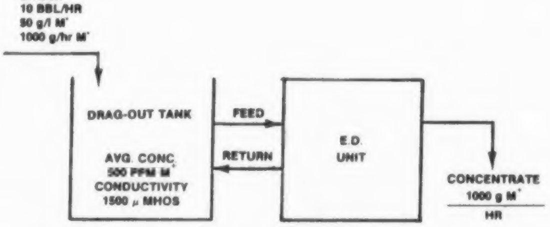

Fig. 2—Schematic of ED Process

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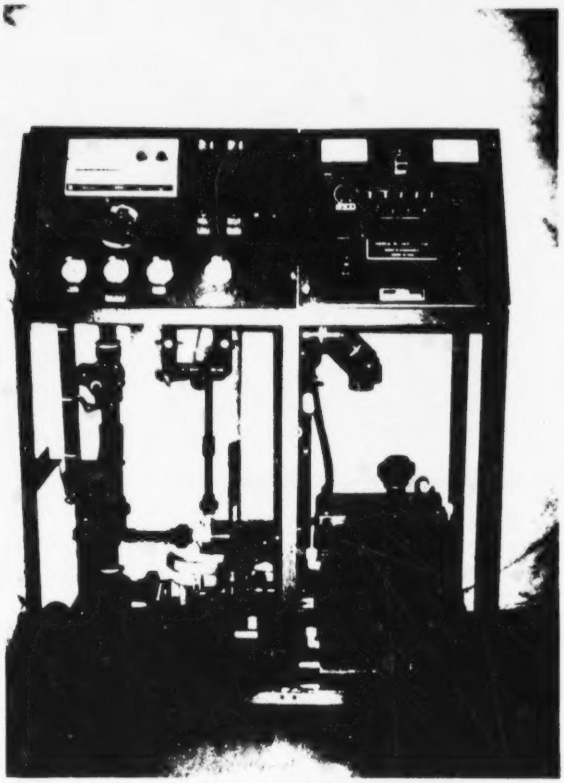

Fig. 3—Operational ED Unit

solutions has produced gold recovery rates over 99%. We have found that gold platers are most resourceful in discovering systems to optimize gold recovery. ED plays a major role in these systems due to low initial cost, low energy consumption, and ability to produce a product suitable for direct recycle to the plating tank.

Circuit-Wise of North Haven, Conn., is one of the larger printed circuit manufacturers in New England. Before they decided on a recovery system for their Mircoplate 7000 Tab Plater, four competing recovery systems were evaluated both by in-plant engineers and by an independent consultant firm. Electrodialysis was chosen as the most applicable process for this installation.

Initially, the ED system was operated on the dragout rinse following the plating station, and a small ion exchange column was installed on the second rinse to recover the last gram of gold. The effectiveness of this system was demonstrated by atomic absorption analysis (AA) on the third rinse which had no detectable gold.

The rinsing in this automatic tab plating machine is very effective and there is very little carryover of contaminants from one process tank to another. Therefore after analysis, the concentrate recovered by ED was returned directly to the plating tank. The system operated in this manner, returning recovered concentrate directly to the plating tank with no buildup of contaminants. Over 35 troy ounces of gold were recovered in the first operation, and with the price of gold at that time, the ED system had paid for itself. Additional savings were building up in the eliminated interest charges which would result from gold in dead inventory on ion exchange resin and at the refiners. Refining charges were also eliminated.

The ED was operated in the constant voltage mode which allows the concentration of the recovered solution to "float", but will recover the maximum amount of gold. Operating in this manner, the concentrate ran from a low of 0.14 troy oz/gal to a high of 5.26 troy oz/gal.

Circuit-Wise ran for 8 months in this manner, recovering over 150 troy ounces of gold. Typical gold concentrations in the recovered solution and amounts of gold recovered are listed in Table 1. **The engineers, encouraged by this performance, looked for ways to recover additional gold** from their wide range of processes.

The culmination of this research is now operating at Circuit-Wise. Gold recovery is enclosed in a separate high security area. Within this room, ED is the heart of the recovery system.

On the production floor, each gold plating area is organized with a dragout tank following the plating station. The second rinse tank is also a dead rinse as is the third rinse. The first dragout rinse is withdrawn into drums periodically to maintain the concentraation of gold below 0.1 oz/gal. The second and third rinses are continuously circulated through separate ion exchange cartridges. When the concentration of gold in the third tank exceeds a pre-set level, the resin on the second tank is retired, the ion-exchange on the third tank is moved to the second, and fresh resin is installed on the third tank. This system effectively recovers over 99% of the gold dragout.

Within the recovery area, the drums containing the dragout solution from each plating line are stored and segregated as to type of bath. When a sufficient quantity has been collected, the solution is concentrated through the ED instrument. Analysis of the stripped solution by AA confirms the complete removal of gold before being sent to waste treatment. The concentrate is also analyzed for gold

Table 1
Gold Concentration of Recovered Solutions From Microplate

	Maximum concentrate Troy oz/gal.	*Minimum Concentrate Troy oz/gal.*	*Average Concentrate Troy oz/gal.*	*Troy ounces Recovered*
December 1980	4.48	0.39	1.22	35.5
January 1981	5.26	0.45	2.11	18.3
February 1981	1.97	0.16	0.98	13.0
March 1981	1.86	0.27	0.98	10.1
April 1981	1.26	0.43	0.79	15.8
May 1981	3.04	0.28	1.43	21.4
June 1981	1.87	0.16	1.01	9.5

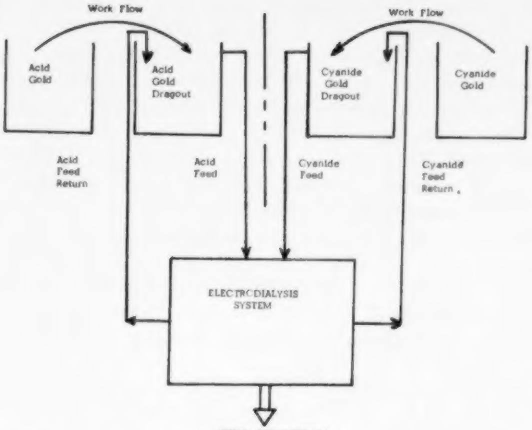
Work Flow
Acid Gold
Acid Gold Dragout
Work Flow
Cyanide Gold Dragout
Cyanide Gold
Acid Feed Return
Acid Feed
Cyanide Feed
Cyanide Feed Return
ELECTRODIALYSIS SYSTEM
GOLD CONCENTRATE

Fig. 4—Recovery system at artistic plating.

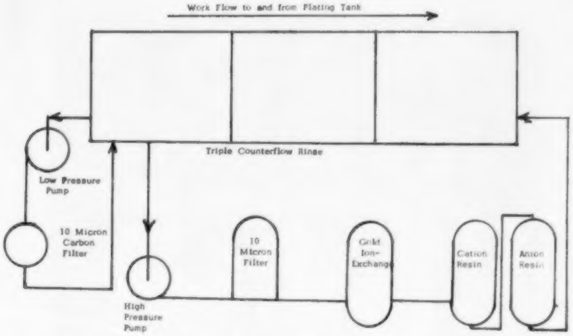
Work Flow to and from Plating Tank
Triple Counterflow Rinse
Low Pressure Pump
10 Micron Carbon Filter
High Pressure Pump
10 Micron Filter
Gold Ion-Exchange
Cation Resin
Anion Resin

Fig. 5—Rinse purification system at artistic plating.

content and then bottled and placed in stock as replenishment solution for the individual lines. The foreman signs out for the recovered solution just as he does for new products. Very close control is kept over the recovered solutions. In the first ten weeks of operation, over 180 troy ounces of gold were recycled directly into the plating tanks. The analysis of these solutions is tabulated in Table 2.

The savings in interest charges due to immediate recycle are significant. Even with an 8-week return of gold recovered by ion-exchange or plating out, there would still be about 150 troy ounces of gold held as unusuable inventory in various stages of recovery. At today's high interest rates, the savings over one year would be over $13,000.

Circuit-Wise also recovers gold from their rejects. After stripping the gold, ED is used to concentrate the gold in the solution to 8 oz/gal for ease of handling and control of gold content. Gold present in ion exchange resin is recovered as a solid after burning off the resin.

Artistic Plating Co.

Artistic Plating Co. Inc. is an upper midwestern job shop specializing in precious metal plating. Of particular interest

Table 2
Analysis of Recovered Solutions—July-Sept. 1981

Lot #	*Volume*	*Concentration*	*Troy ounces*
1	63 l	1.44	24.0
1A	38 l	0.556	5.6
2	68 l	1.39	25.0
2A	54 l	0.28	4.0
3	69 l	0.92	16.8
4	31 l	1.74	14.3
4A	32 l	0.31	2.6
5	36 l	2.23	21.2
5A	36 l	0.37	3.5
6	30 l	3.12	24.8
6A	36 l	0.55	5.2
7	61 l	1.25	20.2
7A	54 l	0.12	1.7
8	43 l	0.98	11.2
			180.1

Table 3
Installation Cost

Components	*Cost*
E D System	$16,000
Pumps	700
Piping	1,000
Controls	1,200
Resins/Filters	650
Installation Labor	1,500
Total	$21,050

Table 4
Annual Operating Cost

Components	*Cost*
Electrical Power	$300
Chemicals	175
Filter Cartridges	150
Replacement Membranes	750
Labor	1,000
Resin (Gold Selective)	70
Resin (H-OH)	900
Total	$3,345

Table 5
Silver Recovery Justification Oneida Ltd.

Operating conditions Before E.D.

Operating Hours	8 hrs./day
Dragout	20,000 Troy oz/yr.
Recovery Method	Precipitation as Silver Chloride

Savings With E.D. Recovery

Cyanide Treatment @ 2.60/#	$ 5,200/yr.
Refining Charges @ $.56/Troy oz.	$11,200/yr.
Interest Charges for Silver at Refiners - 4 months @ 12% Annual Interest	12,800/yr.
Refining Loss 5% Difference between Oneida's Assay and Refiners Return	$16,000/yr.
Total Savings with E.D.	$45,200/yr.
Installed Cost of E.D.	$30,450/yr.,

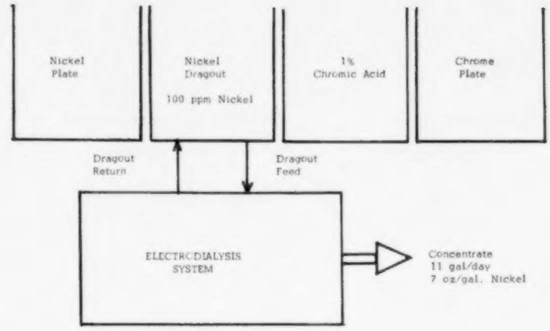

Fig. 6—Recovery system at Stratford Metal Finishing.

is the large volume of plumbing hardware which is gold plated. Seventy percent of their gold consumption is used on a large assortment of plumbing accessories ranging from brass and zinc castings to stainless steel stampings to six foot brass extrusions. Due to the varying nature of the raw materials received for processing, impurity build-up in costly gold baths has been a problem of continuing concern. In the past several years, fluctuations in the cost of raw materials have been no where more dramatic than in the precious metal market where changes of up to 100% have been seen in a matter of months. To combat these problems, Artistic Plating has designed a system which effectively eliminates the buildup of bath impurities and maintains in-house control of all gold recovered.

The closed loop system is designed to recover gold from a drag-out tank, continuously removing impurities and allowing reintroduction of gold concentrate into various baths. It additionally purifies and reuses its rinse water by means of several techniques common in the metal finishing industry. The system is unique in that it uses a closed-loop approach to a plating system generally not thought to be adaptable to that mode of operation.

The heart of the recovery system is the electrodialysis recovery system operated on the dragout rinses. The ED system is piped directly into both the acid gold dragout and cyanide gold dragout. Only one dragout is concentrated at a time. The system is equipped to rapidly flush from itself any residual acid or cyanide remaining before alternating between dragout tanks. The concentrate is collected and available for direct recycle into the plating tanks. This may be seen schematically in Figure 4.

Work being processed in gold plate is rinsed prior to and after plating in the same closed loop counterflow rinse station. This rinse station is continually purified by two separate systems. Organic impurities are removed by continuous filtration through activated carbon. The second system provides a high flow to rapidly circulate purified water for rinsing.

This system is also equipped with a gold selective ion exchange resin to collect any gold which escapes ED recovery.

Removal of solids is accomplished by use of a 10 micron filter. Residual ionic species are removed with an anion-cation H-OH resin. This procedure is demonstrated in Figure 5.

The ED unit is operated as required by monitoring percent conductivity settings on the dragout rinse. The concentrate from this contains over 95% of all recovered gold. This concentrate is analyzed and added as required to gold strike tanks in non-critical, decorative applications, where the main criteria is the appearance of the plate.

The installed cost of the ED rinse system was $21,050. The annual operating cost is $3,345. The initial payback occurred after 9 months of operation. The average gold recovery rate is 3.9 troy oz/month. Although Artistic Plating recognizes the cash flow advantages of direct recycle, they did not directly use this in the payback justification. The complete figures are tabulated in Tables 3 and 4.

ED Application in Nickel Plating

Stratford Metal Finishing of Winston-Salem, North Carolina had a serious problem. Their shop is situated over a stream, and the discharge limits were below 1 mg/l for all metals. The shop has been in existence for many years and the space available for effluent treatment was minimal. In fact, the available space was so small that they did not have room to segregate the nickel rinses from the cyanide-bearing rinses.

This resulted in nickel complexing with the cyanide giving excessive treatment times, chemical usage, and nickel in the discharge.

The solution devised by Stratford Metal Finishing was the treatment of plating rinses to allow recycle of the treated water for use in rinsing. Although Stratford terms their water use "closed loop", there is the inevitable discharge of water to reduce the build-up of dissolved solids. **Occasionally certain solutions such as spent strippers and floor spills are barrelled and shipped to a licensed hauler.**

Electrodialysis plays an important role in the total effluent treatment package. The only way Stratford could have made this system functional was to eliminate nickel mixing with the cyanide in the treatment tanks. They were not as concerned with the recovery value of the nickel solution, as in eliminating nickel from their rinses so their recycle system would work.

The ED was oversized for the amount of nickel dragout expected. This would allow Stratford to operate the ED in the constant voltage mode to effect the greatest extraction of nickel ions from the dragout while allowing the concentration of nickel in the recovered solution to float. The concentration of the recovered solution was unimportant as there was considerable evaporation from the plating tanks, therefore sufficient room for recycle.

ED Application in Chrome Plating

The chrome plating solutions are also operated in a "closed loop". A proprietary membrane separation process is used for the concentration and recovery of chrome plating solutions. The recovered concentrate is used to replenish the plating tanks.

Rinses from the cyanide plating tanks are handled by conventional chemical treatment to oxidize the cyanide and precipitate the metals. Rinses from the cleaning and pickling operations are neutratlized by conventional means also. The entire effluent flow is then passed through a large filter press to remove solids. The clear effluent is then partially deionized through the use of an H-OH ion exchange unit before reuse.

This system does not save any money compared to a conventional system; in fact it costs more to operate. But the peace of mind obtainable by being able to cement over all the drains in the building has been more than worth the expense to the owners.

Table 6
Silver Recovery at Oneida Ltd.

	Silver (Tr. oz/gal.)		*Potassium Cyanide (oz/gal.)*		*Potassium Carbonate (oz/gal.)*	
	Dragout	*Concentrate*	*Dragout*	*Concentrate*	*Dragout*	*Concentrate*
11/11	0.56	4.19	1.9	6.7	1.0	0.47
11/19	0.50	8.0	1.3	4.5	0.45	<.10
11/24	.35	6.4	1.1	6.1	0.55	<.10
11/30	.58	8.2	1.8	6.6	0.60	<.10
12/4	.44	7.0	1.7	7.4	0.40	<.10
12/10	.52	8.3	1.9	6.6	0.45	<.10
12/71	.34	5.7	1.3	8.5		

The description of operation is sure to raise a few eyebrows among the readers of this paper. This method of recycle is not being recommended as general practice. Stratford Metal Finishing was faced with the option of reducing the metal content in the effluent to virtually unattainable levels or closing down. They chose a third option; elimination of all discharge and sealing all the drains in the building. Hard work, constant attention to details, and an owner determined to make the system work have contributed to its success. This example is presented not as an operating recommendation, but only to demonstrate how electrodialysis is contributing to successful recovery and recycle.

In operation, the system consists of a single dragout rinse following nickel plate continuously purified by ED, followed by a 1% chromic acid solution as an activator before chrome plate. Sulfuric acid is added to the dragout tank to maintain conductivity and allow the greatest recovery of nickel. The operation is shown in Figure 6. The 1% chromic acid solution is sent to a licensed hauler about once a month.

This system has been in operation for 6 months. During this period the average concentration of nickel in the **dragout rinse has been below 100 mg/l. On the average a nickel solution at 75% of bath strength is recovered at 11** gallons per 16 hour day. There has been no significant drag-in of nickel or chloride into the chrome plating tank. And there has been no nickel detected in the effluent treatment system.

ED Application in Silver Plating

Oneida Ltd. located in Sherrill, New York is a major manufacturer of silver plated tableware and holloware. As their production increased due to both increased sales and acquisition of new product lines, economical recovery of dragged out silver became a top priority.

The approach taken by the engineers at Oneida Ltd. was very conservative. After evaluating many systems, the most promising were installed for on-site evaluation. As a result of these tests, the equipment justification figures were revised and electrodialysis was chosen as the most promising method. The justification breakdown is given in Table 5. Once the electrodialysis recovery system was installed, periodic analyses were made to determine if the system was living up to expectations. The results of these were tabulated in Table 6. The most interesting item revealed from analyzing this table is the apparent order of recovery of the ionic species.

The major components of a silver bath are silver cyanide, potassium cyanide and potassium carbonate (from the breakdown of potassium cyanide). When the dragout containing these chemicals was passed through the electrodialysis unit, the silver cyanide passed through the membrane in a greater proportion to the potassium cyanide than present in the dragout. The potassium carbonate, which is weakly ionized compared to the cyanides, was recovered in only very small amounts.

The major conclusions that can be drawn from these results are (1) the silver may be recovered at concentrations over 2 times bath strength; (2) carbonates do not tend to be concentrated by electrodialysis; and that (3) the recovered concentrate may be added directly to the plating bath for reuse. Since the dragout is high when plating holloware, the concentration of the highly conductive cyanide ions is sufficient to block the transfer of the carbonate which has been a problem with other direct recycle recovery methods. Thus the concentrated dragout may be directly recycled without fear of accelerated build-up of carbonates.

Electrodialysis systems are also operating on palladium chloride, acid tin (sulfate) and cyanide cadmium. In total, there are more than fifty operating electrodialysis systems in the field, and this total is expected to more than double in 1982. Systems designed for the recovery of fluoborate solutions and chrome plating solutions are expected to be released from development into full production during 1982. The wide range of applications and economical cost have established electrodialysis as the preferred method of recovery for many solutions. The many successful applications in the field will insure its continued growth.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

Electrolytic Metal Recovery Comes of Age

C. A. Swank & W. J. McLay*

Electrolytic metal recovery is one of a growing number of tools available to the metal finisher for recovery of the materials lost in the dragout from his plating tanks. The stringent restrictions on the disposal of metal finishing wastes, and the increasing costs of disposing of sludge created by the metal in these wastes, combine to make recovery of the dragout a very attractive proposition. The most commonly used recovery technologies are: evaporation, reverse osmosis, electrodialysis, ion exchange and electrolytic metal recovery. Each of these technologies has its niche in the field of dragout materials recovery. Two or more of these techniques may also be used in conjunction with one another; for example, ion exchange can be used to concentrate a metal ion from a very dilute rinse stream and the metal can then be electrolytically recovered from the more concentrated regenerant.

The first four of these methods of recovery are all concentrative in nature—they basically remove water, and varying amounts of impurities, from the dragout and produce a concentrate that is available for return to the plating bath. Two problems are inherent in concentrative methods: bath growth and bath contamination. It is almost always the case that when soluble anodes are used, the anode efficiency is higher than the cathode efficiency with the difference ranging up to very high values for some barrel plating lines. The resultant metal buildup is usually more than compensated for by dragout, but when dragout return is practiced, the increase in metal concentration can become a significant problem. Plating baths are normally purged of trace impurities by dragout, but when dragout is artificially reduced, these trace impurities can build up to significant levels. The buildup of impurities can be controlled, however, by the incorporation of purification steps into the recovery system, and the use of high purity water for rinses and bath makeup.

Electrolytic metal recovery is radically different from the other methods of recovery; it is selective, removing only the metal and thus, decoupling the production and recovery processes. Since electrolytic metal recovery doesn't concentrate the dragout and return it to the bath, a properly functioning plating bath will continue to give satisfactory performance after electrolytic metal recovery is put on line. Electrolytic metal recovery does recover the most valuable constituent of the dragout—the metal. The metal is also the component of the dragout that is responsible for the formation of the sludge.

The choice between electrolytic metal recovery and one of the concentrative methods of recovery is basically an economic one. The metal is the most valuable constituent of the dragout from many plating baths, while the cost of replacing the other components is not high enough to warrant the cost of recovering them. In other instances, the metal is relatively inexpensive, and recovery of the entire dragout makes more economic sense. Capital expenditures for the recovery equipment, and the operating costs, must be considered along with the recovery value of the dragout. The complexity of the equipment and the skill required of the operator, as well as the amount of operator time necessary are also important factors in the decision.

Electrolytic metal recovery is not a new technology. The mining industry has used electrolytic means of refining ores for many years, and copper has been recovered from pickling solutions for a significant period of time. In recent years there has been considerable, and increasing, interest in the use of electrolysis for the recovery of metals from dilute rinse waters.

Dilute rinse waters pose a special electroplating problem. The cathode polarization that is the concern of all platers is a much more acute problem for someone who is trying to plate out of a very dilute solution. In general, as plating proceeds, the area of solution next to the cathode becomes depleted in metal ions, forming a polarized layer. The ions must diffuse into and across this layer before they can be plated out. There are fewer ions present in dilute solutions, so the rate of diffusion into and across the polarized layer is much slower, and the layer becomes thicker and more depleted. Severe cathode polarization can lead to poor quality deposits: the formation of dark, powdery, burned areas and trees that can grow across to the anodes and short out the cell. The efficiency at the cathode can be greatly reduced, as the electricity is used to decompose water and form hydrogen gas, instead of plating out the metal. There are a number of ways that the problems associated with cathode polarization can be reduced: by running at a lower current density, adjusting the chemistry and temperature of the solution, and agitating the solution.

When plating is carried out at a low current density, the polarized layer is narrower and metal ions can diffuse into and across it more easily. For a given amount of metal, the

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larger the cathode surface area, the lower the current density necessary to plate out the metal. One way of increasing the cathode surface area is through the use of a large tank with many rows of cathodes and anodes. This approach is cumbersome, at best, and to recover from low concentration rinse waters, hundreds of pairs would be needed. A more practical way to achieve high surface area, in a low volume, is through the use of stainless steel wool or porous carbon as a cathode. There are companies working on both of these approaches. It is easy to remove the metal from dilute solutions this way, but the metal can't be recovered until it is dissolved out of the cathode into a concentrated solution and plated out by conventional methods.

The characteristics of a plating solution can be chemically altered in a number of ways. The concentration of metal ions in the solution can be increased and chemical additions can be made to the solution. For example, electrolytes can be added to improve the conductivity of the solution and grain refiners can be added to improve the quality of the deposit. In addition, when the temperature of a plating bath is elevated, the metal ions in the solution become much more mobile and can diffuse much more rapidly through the polarized layer.

Every plater knows that if he agitates his plating solution or his cathodes he can either plate at a higher current density or lower the concentration of metal in his plating bath. Metal has been electrolytically recovered from waste water containing as little as 100 ppm of metal with the aid of rapidly rotating cathodes.

Many of the potentially favorable adjustments that can be made to an electrolytic recovery system are impractical for a once through system, but can be taken advantage of if a closed loop system is utilized. The first rinse after the plating tank can be isolated and continually recirculated through an electrolytic metal recovery cell. Since the basic recovery solution is being reused, it can be heated, the concentration of metal ions can be allowed to build up to a reasonable level, and other adjustments can be made to the chemistry of the solution.

One electrolytic metal recovery system utilizing rapid agitation of the recovery solution has been used to recover metals from solutions containing as little as 0.04 ppm of metal. The solution is recirculated past the electrodes by impellors located at each end of the cathode compartment. Impellor design has been optimized to provide a uniform flow of recovery solution past the surface of the cathodes. In most cases the reusuable cathodes are of stainless steel, and are provided with edge guards to aid in the removal of the metal deposit. The metal produced with this electrolytic metal recovery cell is of high quality and can either be reused as the soluble anode in the plating tank or sold. The system is basically simple to operate, and once the start-up period is over, requires a minimum of operator time.

Although recovery can be achieved from solutions containing very low metal concentrations, it is usually recommended, for economic reasons, that the concentration of metal ions be kept in the 3-6 g/l range. When recovering precious metals, such as gold and silver, it makes sense to use the extra capacity necessary to maintain the metal concentration on the order of 50-200 ppm in the recovery rinse. Furthermore, when an electrolytic metal recovery cell is used for the recovery of metal from a spent plating bath, the initial metal concentration is high enough that it is often economically feasible to reduce the concentration to levels below 1 ppm.

The electrolytic metal recovery system has been successfully operated on copper sulfate, gold cyanide, silver cyanide, tin/lead fluoborate and many other recovery solutions. Laboratory work has recently been completed on the recovery of copper from a cyanide plating solution, for use with a high speed barrel plating operation. Because of the large difference in cathode and anode plating efficiencies and the large dragout associated with barrel plating operations, a growth in the plating bath was anticipated if dragout return was practiced, and it was felt that an electrolytic metal recovery cell placed on the rinse immediately following the plating bath would be a useful component of this plating system. A five week plating test was done during which dragout to the rinse was simulated by periodically adding small quantities of used copper cyanide plating bath to the solution in the recovery cell. The copper concentration was maintained at an average of 5 g/l, and 365 grams of copper were recovered during 852 ampere-hours of plating. The cathode efficiency was 67%, and 82% of the cyanide added to the system was destroyed.

One of the most common applications for electrolytic metal recovery is the recovery of copper from sulfuric acid solutions. At a GTE/Automatic Electric facility, copper is being recovered from the rinse following a pre-etch solution. Data were collected over a five week period, during which 536 pounds of copper were recovered. The average copper concentration was approximately 5 g/l, and the cathode efficiency was 90%.

Besides being used to recover metal from dilute rinse waters, the electrolytic metal recovery cell can also be used to recover metal from crystals and sludges, and to regenerate process solutions. Data were collected from a GTE/Automatic Electric facility that utilizes an electrolytic metal recovery cell to regenerate a sulfuric acid leach solution. The copper concentration in the leach solution was maintained at an average of 2 g/l, and 86 pounds of copper were recovered in a week at a cathode efficiency of 96%.

Electrolytic metal recovery is one of the most versatile and valuable tools available to the plater for the recovery of metal wastes generated in a plating shop. It has minimal impact on the production line when it is used for the recovery of dragout, and it can be applied to recovery from other areas in the plating shop. Electrolytic metal recovery is not universally applicable as a recovery technology, but in many cases it is the most economical alternative available when the metal value is much higher than that of the other components of the bath, and when capital costs of the equipment, operating costs, and time and skill required of the operator are taken into account.

The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

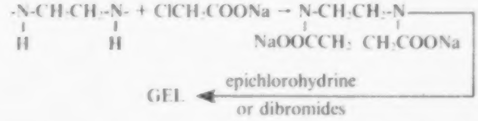
New Developments For the Treatment of Wastewater Containing Metal Complexers

Dr. C. Courduvelis, G. Gallager, & B. Whalen

Several existing technologies are available to treat metal bearing wastewaters. The simplest, is conventional alkaline precipitation using caustic or lime. This process is inhibited by the presence of some complexing agents, which keep the metal salts in solution. Processes to precipitate metals in the presence of complexing agents such as insoluble starch xanthate (ISX), ferrous sulfate, cellulose xanthate, hydrogen peroxide, sodium hydrosulfite, and sodium borohydride have been developed. All of these processes use expensive chemical precipitants, which convert the metal to a sludge, requiring dewatering and discarding.

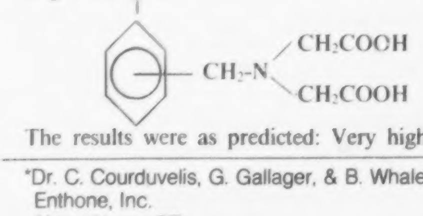
We now have developed a process employing ion exchange resins to remove heavy metals from wastewaters in the presence of complexers or chelators (U.S. Patent No. 4,303,704). The process has the simplicity, convenience, and the low cost enjoyed by the water softening processes, and we expect it to receive wide acceptance in the plating and surface finishing fields. This development has been delayed because these specialty resins have only recently been available for industrial use.

It seemed to reason that a resin with chelating groups would prefer heavy metals to sodium or a chelator. This resin could take a metal away from its complexer if the complexer's chelating or stability constants are less than the chelating constant of the functional group of the resin. This led us to prepare resins by reacting polyethyleneimines with chloracetic acid and cross-link the "comb-like" polymer, which structurally resembles the powerful chelator EDTA.



$$\underset{H}{-N}-CH_2CH_2-\underset{H}{N}- + ClCH_2COONa \rightarrow \underset{NaOOCCH_2}{N}-CH_2CH_2-\underset{CH_2COONa}{N} \xrightarrow[\text{or dibromides}]{\text{epichlorohydrine}} \text{GEL}$$

The approach failed. Cross-linking of this highly hydrophylic polymer created a thick gel, preventing liquid flow. Soon afterwards, a commercial chelating resin became available. The resin is a cross-linked polystyrene bearing iminodiacetic acid functional groups:



The results were as predicted: Very high efficiency for removing copper from an electroless copper solution. (Electroless copper contains copper sulfate, a chelator, and a large quantity of sodium ions.) Under proper conditions the effluent contains less than 1 ppm of copper, the "free chelator", and sodium.

The resin is packed in a column and the electroless copper solution is passed through at an appropriate rate and pH. The copper is held on the column and the solution containing the chelator is passed through and can be discarded. After the resin is exhausted it is regenerated with dilute sulfuric acid which redissolves the copper retained on the resin. This copper bearing acid solution can be treated with sodium hydroxide or lime to precipitate the copper quantitatively into very pure copper hydroxide, or to plate it out and recycle the acid to be used in the next regeneration. Another application of ion exchange resins for recycling the copper and chelator from electroless coppers has been described by Zeblinski.[6]

Chelating resins are the only resins which seem effective for this process. Typically, cation-exchange resins prefer sodium over a heavy metal. The small amount of heavy metal which is captured on it is accompanied by its chelator. Both the metal and the chelator then are dissolved together

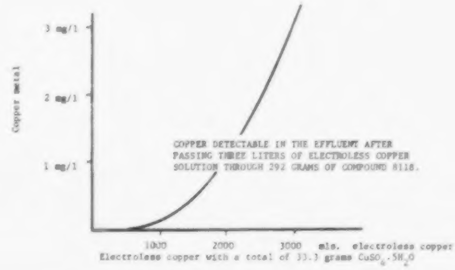


Figure 1-1.

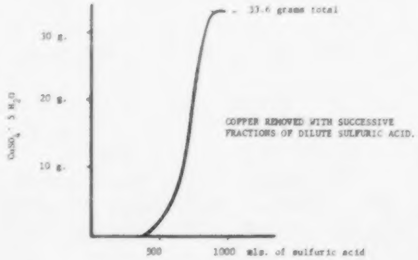


Figure 1-2.

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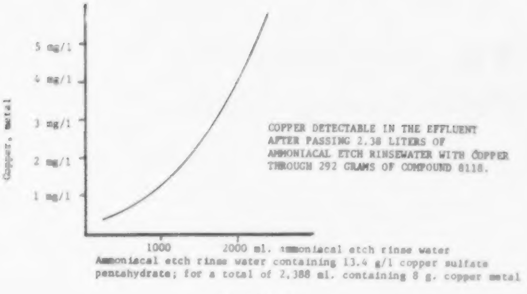

Figure 1-3.

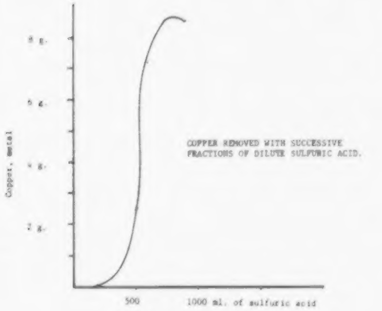

Figure 1-4.

in the acid or sodium hydroxide when the resin is regenerated, making metal precipitation impossible. Anion-exchange resins have no chemical affinity for heavy metals. Perhaps with polar interaction a few can tie some heavy metals. Again, the metal takes its chelator along making precipitation impossible.

Areas where the process can be applied:

1. Electroless copper.
   a. Pass the water rinses contaminated with electroless copper through the chelating resin at adjusted pH to remove the copper before discarding.
   b. Recycle such rinses by recirculating through the resin to maintain low copper level.
   c. Pass the spent electroless copper solutions and bailout directly or after plating out the bulk of the copper.
2. Etchants of printed circuits containing copper. Ammoniacal, persulfate or perioxide based etchants and their rinses.
3. Electroless nickel.
   Both the rinses and spent electroless nickel solution.
4. Various electrolytic copper or nickel rinses and solutions.

Types of complexers or chelators that can be present

Besides ammonia a variety of other complexers or chelators can be present together with the copper or nickel in the solution to be treated.

a. Copper can be separated from carboxylic acid type chelators like tartrates, and nickel from citrates, gluconates, lactates, and cuccinates, etc.
b. Copper can be separated from alkanolamines like tetrakis-(2-hyroxypropyl) ethylenediamine, (quadrol), tetrakis-(2-hydroxyethyl) ethylenediamine, triethanolamine, etc.

No separation of copper takes place in the presence of ethylene-diaminetetraacetate (EDTA), nitrilotriacelate (NTA) and other aminoacid type chelators.

The results appear to agree with the expectation based on the chelating constants. Thus, the iminodiacetic acid group of the resin with chelating constant $K=10^{10.55}$ (7) will take away the copper from quadrol, which has a lower chelating constant for copper, $K=10^{9.2}$ (8) and from tartaric acid, $K=10^{9.9}$ (7) but not from EDTA, $K=10^{18.8}$ (7) and NTA, $K=10^{12.68}$ (7).

The efficiency for copper separation from quadrol is greater in an acidic solution, pH=2.2-7.0, than it is in an alkaline solution. This can be due to the fact that in alkaline solutions the quadrol becomes a stronger chelator, as it has been reported elsewhere.(9)

EXPERIMENTAL DATA

Example 1: Electroless Copper

A glass column of 4 cm diameter was charged with 292 grams of Compound 8118* to 30 cm height. A solution of spent electroless copper containing 11.1 g/l $CuSO_4 \cdot 5H_2O$, 25 g/l NNN'N-tetrakis-(2-hydroxypropyl) ethylenediamine complexer, 8 g/l free sodium hydroxide, 14 m/l of 37% formaldehyde, and 60 g/l each of sodium sulfate and sodium formate was acidified to pH 2.5 by addition of 18 ml of sulfuric acid per liter and passed through the resin at a rate of 12 ml/min. The results of the copper removal are shown in the Figure 1-1.

The various fractions of the effluent contained from 8.3 - 15.6 g/l of complexer NNN'N'-tetrakis-(2-hydroxypropyl) ethylenediamine.

The column was rinsed with water and eluted with 4% volume sulfuric, which was passed at the same rate, 12 ml/min. The results are shown in Figure 1-2.

When made alkaline (pH 9-10), the copper in the eluant was easily removed.

Example 2:

Continuous Removal of Copper from Electroless Copper Rinses - Recycling of the Rinse

The same set up of example 1 was used to remove copper continuously from a rinse water of 6 liters which was contaminated by continuous pumping of 0.36 ml/minute of an electroless copper solution containing 2,375 ppm of copper. This is a 1:100 scale-down of the operating conditions of an existing plating on plastics installation. The continuous removal of the copper was achieved by continuous pumping of the rinse water through the column at pH 3.5-4.0. If V is the volume of the rinse passing through the column per minute and if the V volume looses all of its copper during passage, then V x G = (0.36) x (2375), where G is the concentration of the copper in the rinse. Thus G will remain constant for a given value of V. This G is the concentration at steady state equilibrium.

We established 43 ppm of copper in the rinse, yielding V equal to 20 ml/minute as the rate of recirculation.

The system was operated continuously for 6 x 24 hour days. During this time the rinse was analyzed by Atomic Absorption Analysis and found to contain between 25 and 35 ppm of copper, while the solution returned from the resin to the rinse had less than 1 ppm of copper. The experiment was continued for one more day where the copper level in the rinse rose to a final 52 ppm and the returning from the column water had 5 ppm of copper. A total of 3050 ml of electroless copper was pumped into the rinse indicating 7.2 g of copper. Since 6 liters of rinse x 52 ppm = 0.3 grams of

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*A chelating resin.

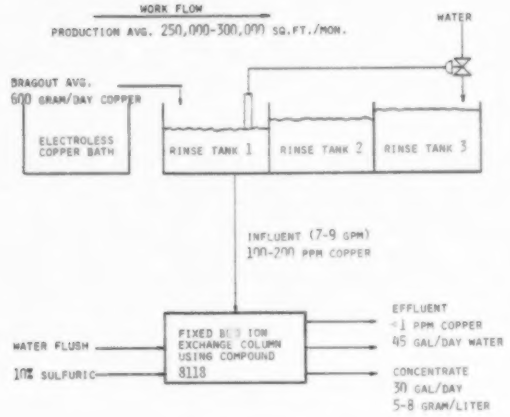
WORK FLOW
PRODUCTION AVG. 250,000-300,000 SQ.FT./MON.
WATER
DRAGOUT AVG.
600 GRAM/DAY COPPER
ELECTROLESS COPPER BATH
RINSE TANK 1
RINSE TANK 2
RINSE TANK 3
INFLUENT (7-9 GPM)
100-200 PPM COPPER
WATER FLUSH
10% SULFURIC
FIXED BED ION EXCHANGE COLUMN USING COMPOUND 8118
EFFLUENT
<1 PPM COPPER
45 GAL/DAY WATER
CONCENTRATE
30 GAL/DAY
5-8 GRAM/LITER

Fig. 2-1—Overall Schematic of I.X. Column Operation.

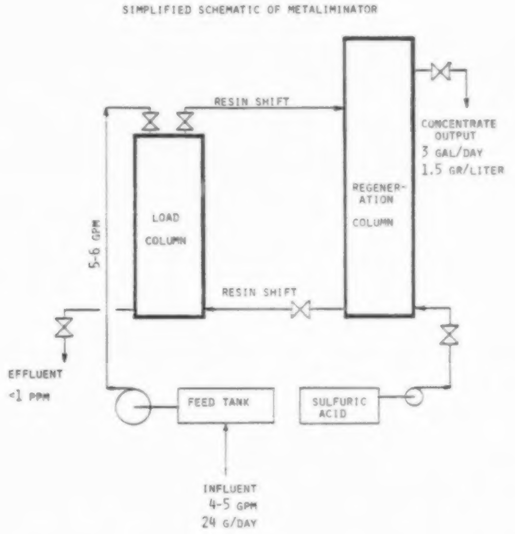
SIMPLIFIED SCHEMATIC OF METALIMINATOR
RESIN SHIFT
CONCENTRATE OUTPUT
3 GAL/DAY
1.5 GR/LITER
LOAD COLUMN
REGENERATION COLUMN
5-6 GPM
RESIN SHIFT
EFFLUENT
<1 PPM
FEED TANK
SULFURIC ACID
INFLUENT
4-5 GPM
24 G/DAY

Figure 2-2.

Table 2-1
Advantages and Disadvantages of Fixed Bed Ion Exchange Using Compound 8118

Advantages

1. Consistent effluent quality of less than 1 ppm copper.
2. Low space requirements.
3. Low energy costs.
4. Columns can be designed to handle a broad range of flowrates.
5. Extremely low treatment chemical costs.
6. When considering equally effective treatment options, comparatively low capital cost.

Disadvantages

1. Incapable of handling certain chelator systems.
2. Downtime required to regenerate columns unless there is a spare column.
3. Incapable of handling concentrated solutions at high flowrates.
4. Column size, and therefore cost, is flow and copper concentration dependent.
5. Distributors can become clogged with resin, requiring periodic cleaning.

Table 2-2
Advantages and Disadvantages of The METALIMINATOR

Advantages

1. Consistent effluent quality of less than 1 ppm copper.
2. Low space requirements, 2' x 4' x 6.5'.
3. Comparatively low capital cost.
4. Extremely low treatment chemical cost.
5. Continuous - on line operation.
6. Less resin required.

Disadvantages

1. Uncapable of handling certain chelator systems.
2. Flow limitations, less than 9 gpm.
3. Lower concentration of copper in the spent regenerant (concentrate).
4. Access is difficult to distributors when periodic cleaning is required

copper, the column had retained 7.2-0.3 = 6.9 g in 292 g of resin. The 6 liter volume of the rinse was maintained by periodic removal of portions of the rinse. Elution with acid was done as in example 1.

Example 3: Ammoniacal Etch

Rinse water containing 13.4 g/l $CuSO_4 \cdot 5H_2O$ fully complexed with ammonia at a pH of 11.5 was acidified to a pH of 4.0 and run through the column described in example 1 at 13 ml/min. The effluent fractions had the copper content shown in Figure 1-3.

The column was eluted with 4% vol. sulfuric acid, yielding the following as shown in Figure 1-4.

Example 4: Electroless Nickel

Electroless nickel solution containing 9 g/l Ni, 100 g/l sodium citrate, 50 g/l ammonium chloride, 10 g/l of sodium hypophosphite at pH 8.3 was passed through the same column of example 1 at 14 ml/l. The first fraction of 600 ml had less than 1 ppm of Ni (in this case, 5.4 grams of Ni has been retained by 292 grams of resin). The next fraction of 200 ml had 3 ppm of Ni and the 3rd fraction of 250 ml had 46 ppm. The column was rinsed with water and eluted with 4% vol. sulfuric acid. The first 245 ml had about 20 ppm of nickel and the following fractions, a total of 800 ml, contained the bulk of the nickel, which varied from 4 to 26 g/l. The tail fraction of about 500 ml contained a few ppm.

Treatment of the combined eluants with sodium hydroxide precipitated the nickel quantitatively. The remaining filtrate had only 0.4 ppm of nickel.

FIELD DATA

Research in the laboratory led to the development of a patented process utilizing Compound 8118 by which copper and nickel could be removed from most complexers in solution. The next phase was to field test this process. The objective of the field test work was to design a full scale system utilizing the patented process which could operate under plant conditions. We wanted to examine the system's ability to efficiently and effectively remove copper from chelators in solution. The success of this was determined by a copper concentration of less than 1 ppm in the effluent. Additionally, we hoped the metal that was retained on the resin could be extracted with a small volume of sulfuric acid, yielding a concentrated solution. This would facilitate easy handling of the concentrate. This concentrate could either be precipitated as a hydroxide or carbonate, or the metal could be electrolytically recovered.

The first major field application of this process was in 1980 at a large plating on plastics (POP) facility. There was an effective waste treatment system handling their existing wastewater, but they were committed to adding electroless copper plating to their POP cycle. The existing system was not capable of handling this waste stream. A fixed bed ion exchange (IX) system using Compound 8118 was designed and installed to accomplish two purposes: (1) prevent the chelator in the electroless copper from upsetting the existing treatment system, and (2) remove the copper in the electroless copper wastestream to below 1 ppm (mg/l).

Figure 2-1 illustrates the plating bath and rinse tank arrangement, the input and output from the ion exchange columns, the volume of regenerant used, and the concentration of copper in the regenerant.

The rinse tanks were modified to take advantage of counterflow rinsing. Production was highly variable and therefore the amount of dragout varied considerably. The dragout from the electroless copper bath averaged 600 grams per day (2 shifts per day). The water in the first rinse tank was constantly pumped through a cartridge filter to the two IX columns. These columns held seven cubic feet of Compound 8118 each. The influent copper concentration varied between 100-200 ppm (depending upon production). The effluent from the column contained less than 1 ppm copper consistently. This water no longer contained copper but still retained the "free" chelator, therefore it was not combined with any other waste streams until after treatment.

As previously explained, the copper was retained on the resin, the chelator was not. When the ion exchange columns became exhausted, they were first flushed with fresh water to displace any chelate-bearing solution that had remained in the column (the hold-up volume) and then regenerated with dilute sulfuric acid to remove the copper ions. This regeneration cycle was initiated by an attendant, and automatically followed a sequence of steps. The columns were regenerated during periods of production downtime, such as the graveyard shift, weekends, etc. Approximately 30 gallons of sulfuric acid were used each time the unit was regenerated. This produced a concentrated solution with 4-8 grams per liter of copper.

Table 2-1 outlines the advantages and disadvantages of using this type of system on rinsewater.

In an effort to overcome some of the limitations of the fixed bed ion exchange system, the search continued for more suitable hardware. In late 1981 a unique moving bed system was brought to our attention. The fixed bed IX unit could only achieve continuous operation by providing a duplicate column. The moving bed system allowed for simultaneous sorption and regeneration, permitting continuous on-line operation. With more frequent regenerations, the volume of resin required became smaller. This reduced the capital cost of implementing the process.

Figure 2-2 illustrates the input and output from this fully automatic, continuously operating IX unit.

The unit was set up to handle the dragout from an electroless copper bath, plating 1000 square feet of laminate per day. Dragout was estimated to be 25 grams per day of copper, and the rinse water flowrate was 4-5 gpm. Fluid is pumped at 5-6 gpm from a feed tank through the load column, and exits with less than 1 ppm copper in the effluent. At the same time sulfuric acid is introduced into the regeneration column. The sulfuric solution moves up through the resin in the column progressively stripping the copper from the resin. The concentrate output has approximately 1.5 gram/liter of copper, which can be easily treated by conventional methods. The copper can be precipitated as copper hydroxide or oxide, or recovered electrolytically (or through immersion plating). Both the rinse water treatment and the resin regeneration continue until they are momentarily stopped by an automatic timer. When this happens, the clean resin at the bottom of the regeneration column is shifted to the load column; and the contaminated resin at the top of the load column is shifted to the regeneration column. This procedure takes only seconds.

The unit automatically returns to removing copper from the rinsewater, and regenerating the copper-laden resin.

Table 2-2 outlines the advantages and disadvantages of using this with Compound 8118 (now called the METALIMINATOR).

This process has also been successfully tested on ammoniacal final etch rinse water, and electroless nickel rinse water.

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Batch Hydrolysis System for the Destruction of Cyanides in Electroplating Effluents

AES Research Project 53

R. G. W. Laughlin, H. L. Robey, and P. S. Gooderham*

ABSTRACT

AES Research Project 53 investigated the effectiveness of simple hydrolysis for the destruction of cyanides in electroplating wastewaters. Hydrolysis was accomplished in a batch system for more concentrated cyanide wastes and in a continuous flow system for dilute rinse solutions. Cyanide destruction efficiencies of greater than 99.9% were achieved at temperatures ranging from 150-250° C on a variety of different plating wastes.

As a follow-up to this project, the American Electroplaters' Society is supporting a commercial demonstration of the batch system. This plant is being built by WetCom Engineering Ltd. and will be installed and tested at Whyco Chromium Co. Inc. in Thomaston Connecticut, early in 1982.

This paper will summarize the laboratory test results and outline the design of the commercial scale demonstration unit.

BACKGROUND

Alkaline cyanide baths have found favour in the electroplating of metals, especially copper, zinc and cadmium, because of their relatively low cost, ease of operation, superior plating ability and excellent throwing power. The wastes generated, however, pose a severe environmental hazard and strict government regulations have been established to restrict the discharge of these wastes.

A variety of processes have been developed for the treatment of cyanide-containing wastes. Alkaline chlorination of cyanide-bearing wastes has been the accepted method of cyanide destruction for about twenty years. In this process, cyanides are first oxidized to cyanates and then to carbon dioxide and water. More recently, processes have been described using ozone[1]; a combination of a peroxide and formalin[2]; a packed-bed electrode[3]; and a catalytic conversion process.[4] Drawbacks to these methods may include high capital outlay, incomplete cyanide destruction or expensive operating costs for treatment chemicals.

In late 1977, the Ontario Research Foundation (ORF) conducted a series of tests on the hydrolysis of cyanides to ammonia and formate as a method for complete cyanide destruction without the use of expensive chemicals. Heisse and Foote[5] reported 65% conversion of cyanide to formate at up to 150° C, ~ 93% conversion at 150° C to 200° C and essentially complete conversion at temperatures in excess of 200° C. The hydrolysis reaction proceeded as follows:

$$CN^- + 2\,H_2O \rightarrow NH_3 + HCOO^-$$

Batch, semi-batch and continuous-flow pilot plant tests were performed at ORF on sodium cyanide, cadmium plate tank waste, copper cyanide plate tank waste and copper stripping solution at temperatures from 188° C to 275° C. The minimum destruction of cyanide achieved in 60 minutes was 98.75%. In almost all of the tests at the higher temperatures, removals of greater than 99.99% were obtained in 60 minutes.

AES Research Project 53 was initiated to confirm the findings of these tests and to determine the economic viability of the process.

RESULTS OF LABORATORY TESTS

A number of cyanide wastes were tested in Project 53, and a significant difference was found in the rate of hydrolysis. The process conditions required for removal of total cyanide to less than 1 mg/L ranged from 200° C and 1.7 MPa (250 lb/in²) to 275° C and 6 MPa (900 lb/in²). The most resistant wastes were found to be spent copper plating solutions and potassium ferricyanide. Test data for these wastes are shown in Figures 1 and 2.

Three tests were undertaken on specific wastes from the plant in which the demonstration unit is to be installed. The streams tested were as follows: a nickel stripping solution

Table 1
Cyanide Removal From Nickel Stripping Solution at 235° C and 550 psi

Reactor Residence Time (minutes)	Total Cyanide Concentration (mg/L) Batch Process	 Continuous Process
Feed	50,000	300
0	12,000	300
15	2,000	50
30	300	10
60	10	0.2
90	0.2	0.01
120	0.01	—

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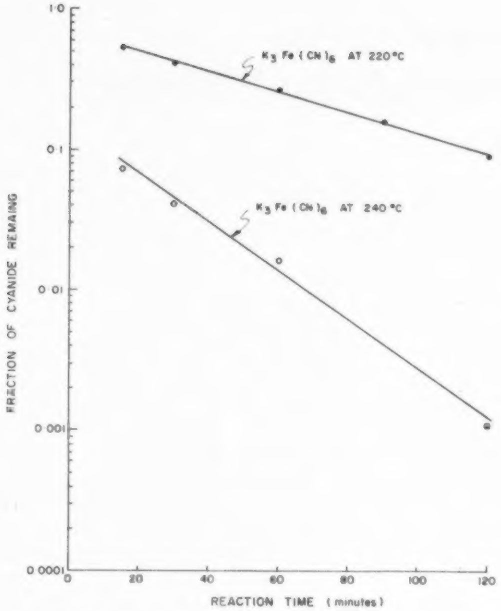

Fig. 1—Hydrolysis of Potassium Ferricyanide (from AES Project 53 Final Report).[6]

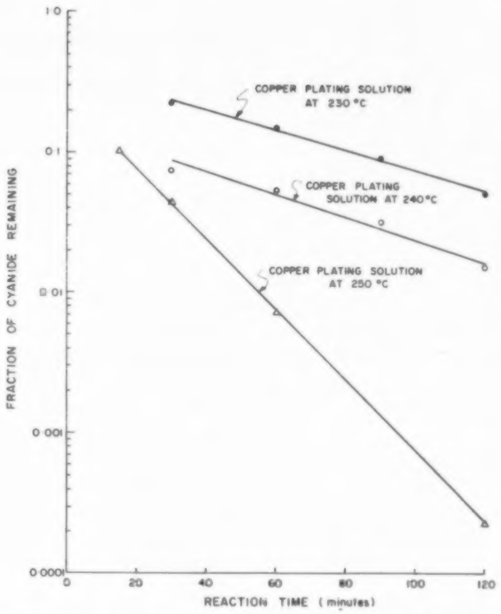

Fig. 2—Hydrolysis of Copper Plating Solution (from AES Project 53 Final Report).[6]

with 60,000 mg/L of total cyanide; an alkaline descaler with 45,000 mg/L; and a mixture of the two wastes with about 50,000 mg/L. Batch tests were run on the three streams at full strength. Continuous flow tests were run on the individual wastes diluted to 300 mg/L of total cyanide to simulate rinse solutions. The results of these tests are shown in Tables 1, 2 and 3. The tables show that acceptable cyanide levels can be achieved with 2 hours or less residence time at temperatures of 250° C or less.

Figure 3 shows the performance for nickel stripping solution at 235° C compared to predicted results from previous tests on nickel cyanide waste at 230 and 240° C. The observed results match the predicted results from previous experiments.

The destruction of cyanide in the hydrolysis reactor solves one part of the plating waste problem. The other concern, which must be addressed, is the removal of soluble metals from the treated solution. The effluent from the tests on the mixture of nickel stripper and alkaline descaler was treated by pH adjustment and by adding sodium sulfide. Metal analyses after the various treatment steps are shown in Table 4. Although large reductions in the concentrations of soluble metals were achieved during the hydrolysis reaction itself, sulfide precipitation was necessary to achieve acceptable effluent levels of soluble zinc and cadmium. Investigations of alternate approaches to zinc and cadmium precipitation are planned during the demonstration project.

The exhaust gas from the hydrolysis of the mixed waste contained 300 ppm of hydrocarbon (measured as methane). This hydrocarbon component is most likely formic acid or ammonium formate produced from the breakdown of cyanide. The gaseous effluent from the process will be investigated as part of the demonstration programme.

DESIGN OF THE DEMONSTRATION UNIT

As a follow-up to the laboratory programme, the American Electroplaters' Society agreed to fund a commercial demonstration of the batch treatment system, for high strength cyanide wastes, at Whyco Chromium's plant in Thomaston, Connecticut. In anticipation of this demonstration project, the wastes investigated during the laboratory programme were from Whyco Chromium Co.

Table 2
Cyanide Removal from Alkaline Descaler at 247° C and 600 psi

Reactor Residence Time (minutes)	*Total Cyanide Concentrations (mg/L)*	
	Batch Process	*Continuous Process*
Feed	50,000	300
0	12,000	300
15	2,300	60
30	450	15
60	15	0.5
90	0.6	0.02
120	0.02	—

Table 3
Performance of Bath Hydrolysis Process on Mixture of Nickel Stripping Solution and Alkaline Descaler at 242°C and 550 psi

Reactor Residence Time (minutes)	*Total Cyanide Concentration (mg/L)*
Feed	50,000
0	12,000
15	2,000
30	400
60	30
90	1.5
120	0.1

Table 4[7]
Effect of Hydrolysis on Soluble Metal Concentrations*

		Metal Concentration (mg/L)			
Metal	*Detection Limit*	*Raw Cyanide Solution*	*Hydrolysis Effluent*	*Hydrolysis Effluent After pH Adjustment to 9.2*	*Hydrolysis Effluent After pH Adjustment to 9.2 and Na_2S Precipitation*
Iron	~ 1	4500	312	264	73
Copper	~ 0.5	3500	0.75	0.6	N.D.
Cadmium	~ 1	2200	800	440	1.2
Zinc	~ 0.5	800	62.5	60.0	0.72

*Test performed on a 50/50 mixture of nickel stripping solution and alkaline descaler

Since this unit is to be a demonstration unit, it has been designed with additional features and an extended range of operating conditions over what might be anticipated for day to day commercial operation. It is designed to be capable of operating at temperatures up to 275° C and pressures up to 900 psi. These conditions were selected on the assumption that the unit should be capable of reducing **50,000 mg/L of the most resistant cyanide, e.g. potassium ferricyanide, to less than 1 mg/L in 2 hours or less. Table 5** shows that 275° C would be sufficient to achieve these rates of destruction.

The initial design concept was for a batch unit capable of processing 250 U.S. gallons/day of concentrated liquid cyanide waste in two batches of 125 U.S. gallons each. The design was based on all of the wastes being pumpable. Discussions with Whyco Chromium Co. suggested that one of their major problem wastes is a solidified cyanide containing sludge, particularly sludge from the bottom of the alkaline descaler bath. This is removed from the bath into 55 gallon drums, where it solidifies. In order that these solidified wastes could also be treated in the batch reactor, the reactor design was modified to allow it to accept a 55-gallon drum. Although the mechanical design of the vessel is more complex with this feature, it was felt that the additional versatility for this demonstration project justified the necessary modifications.

Figure 4 shows a general assembly of the batch reactor system. In order to completely immerse a 55-gallon drum plus the immersion heaters used to heat up the unit, a reactor liquid capacity of 150 U.S. gallons is required. To account for the volume expansion of water at 275° C of 31.5%, and allowing an additional freeboard of 15%, the total reactor design capacity was established at 230 U.S. gallons.

The minimum inside reactor diameter required to accommodate a 55-gallon drum and the heating coils plus other reactor internals is 30 inches. The total internal reactor height from the bottom of the ASME elliptical head **to the top flange required for the design capacity is 83.25 inches. Other system dimensions are shown on the general** assembly drawing in Figure 4. Other design considerations are discussed below:

Materials of Construction

The batch reactor and associated valves and piping will be constructed of type 316 stainless steel for corrosion resistance. To evaluate potential construction materials for future applications, the following four corrosion coupons will be supported in the reactor:

- 304 stainless steel
- 304 L stainless steel
- 316 stainless steel
- mild steel

As part of the process evaluation programme, these coupons will be inspected after 6-8 weeks of reactor operation.

Drum Loading System

Loading and unloading of the drums will be accomplished using an overhead crane and monorail system. The drum will be manually lifted into a "cradle" designed to contain the drum and inserted into the reactor. A stainless steel grid will be placed over the drum to avoid

Table 5
Batch Process Conditions for Treating A Potassium Ferricyanide or Copper Stripping Solution Containing 50,000 mg/L Total Cyanide

	Operating Temperature Required (° C)		
Time at Temperature (hours)	*To Achieve Total Cyanide in the Effluent of Less Than 10 mg/L*	*To Achieve Total Cyanide in the Effluent of Less Than 1.0 mg/L*	*To Achieve Total Cyanide in the Effluent of Less Than 0.1 mg/L*
1	272	280	284
2	256	262	266
3	247	252	256
4	240	245	251

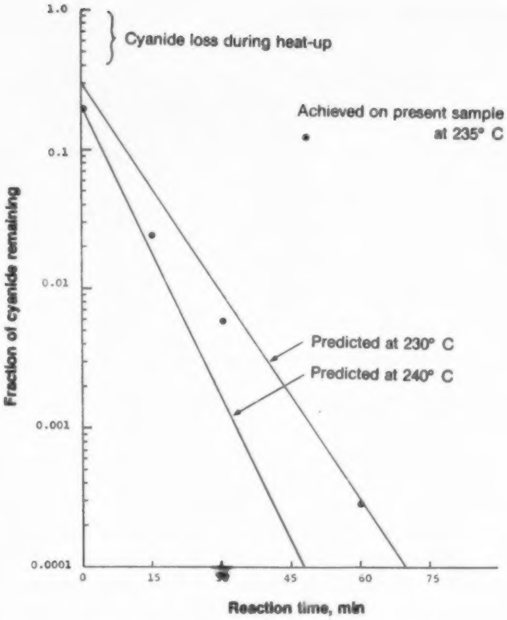

Fig. 3—Hydrolysis of Nickel Stripping Solution Compared to Predicted Results from Tests with Pure Nickel Cyanide.

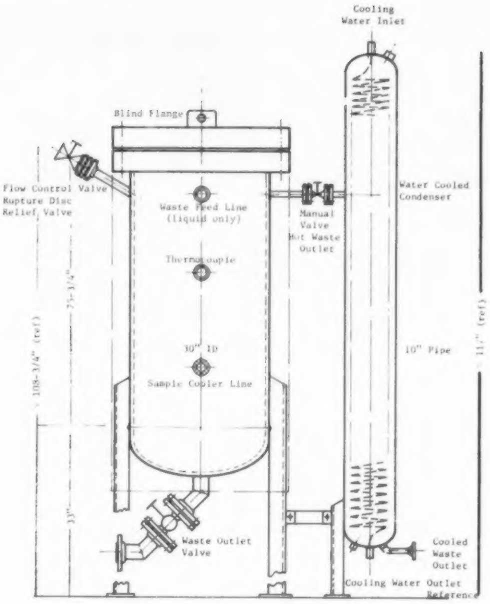
Cooling Water Inlet
Blind Flange
Flow Control Valve
Rupture Disc
Relief Valve
Waste Feed Line (liquid only)
Thermocouple
Manual Valve
Hot Waste Outlet
Water Cooled Condenser
30" ID
Sample Cooler Line
10" Pipe
108-3/4" (ref)
75-3/4"
33"
Waste Outlet Valve
Cooled Waste Outlet
Cooling Water Outlet
Reference

Fig. 4—Bath Reactor—System General Assembly.

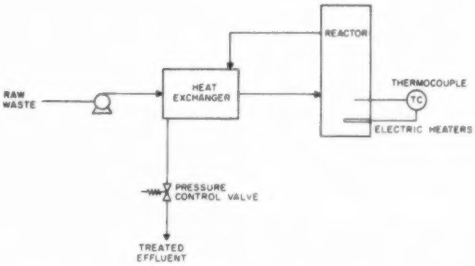
RAW WASTE
HEAT EXCHANGER
REACTOR
THERMOCOUPLE
TC
ELECTRIC HEATERS
PRESSURE CONTROL VALVE
TREATED EFFLUENT

Fig. 5—Continuous Process Flowsheet.

any small plated parts contained in the solidified waste from "boiling over" into the reactor. The crane and monorail will lift the drum, position it over the reactor, and then lower it into position in the reactor.

The drum cradle and top grid, as well as a thermocouple inserted into the solid waste, will remain in the vessel throughout reaction.

Process Heating System

To heat the reactor plus the 150 U.S. gallons of cyanide wastes from ambient to 275° C requires an energy input of approximately 675,000 Btu. This energy could be electrically supplied using either external wall mounted or internal immersion heaters. External heaters are inefficient and may cause baking of the waste on the inside reactor wall. Thus, internal immersion heaters were chosen for this application.

The limiting factor in specifying the power rating of the immersion heaters was found to be the space available to physically locate both the heaters and a drum within the reactor. With this limitation, a heater ouput of 54 kW was specified. This would supply about 185,000 Btu/hour which suggests a nominal heat-up time of 3-½ hours.

A number of physical and chemical factors may influence the heat-up time. The actual heat-up time required will be determined as part of the demonstration programme.

Introduction of a drum of solidified cyanide waste into the reactor makes the prediction of heat-up time more complex. In a liquid phase reactor, one assumes good thermal mixing and fairly even temperatures in the body of the liquid waste. In the case of a liquid containing a drum of solid material, a number of uncertainties must be considered:

(a) The solubilization characteristics of the solid waste with temperature are not known. Thus, it is not known at what point in the heat-up the predominant heat transfer mechanism changes from conductive to convective.
(b) The thermal conductivity of the waste is not known.

Temperature control of the system will be achieved through a thermocouple mounted in the liquid phase close to the wall of the reactor, feeding a signal to a controller on the heaters. This same control system will be used when either liquid or a drum is being processed. During the demonstration programme, data on heat transfer in drums of solidified cyanide waste will be generated by installing a thermocouple into the centre of the drum. Time/temperature profiles will be recorded from the output of this thermocouple. Once the heat transfer process is understood, this thermocouple will no longer be needed, and this would not be a feature of subsequent commercial units.

Cooldown System

The reactor and its contents will be cooled from operating temperature to ~ 100° C by flashing-off water at the end of reaction. Steam released will exit the reactor via a manually controlled valve and pass through a water cooled condenser as shown in Figure 3. Approximately 40 U.S. gallons of water must be evaporated to remove the necessary heat from the system.

A cooldown time of 30-60 minutes is expected.

Ammonia Letdown System

Every mole of cyanide that is destroyed produces one mole of gaseous ammonia. Assuming that this ammonia does not completely react with water to form ammonium hydroxide, the gas will have to be vented during reaction. This will be accomplished in the batch demonstration unit by an automatic pressure control valve.

The maximum flowrate through this valve depends heavily on the amount of gaseous ammonia that is actually released from the aqueous phase, and the amount of water vapour that is stripped by the ammonia gas. Because of the uncertainties outlined previously, the valve has been designed very conservatively, based on our worst experience in laboratory batch scale tests. A more accurate determination of the ammonia released in the reaction will be an important part of the demonstration programme.

Reactor Pressure Relief System

The reactor pressure relief system consists of a rupture disc (set at 925 psig) and a relief valve (set at 900 psig) connected in series. The logic of this is as follows: If the pressure rises to 925 psig, the rupture disc will "crack", and the pressure will drop rapidly to 900 psig, and will be held at this by the pressure relief valve. The approach prevents a complete evacuation of the vessel contents.

PROCESS DEMONSTRATION PROGRAMME

The start-up of the batch demonstration unit is scheduled for January/February, 1982. Tasks to be undertaken during the demonstration phase of the programme include:

- comparison of full scale performance predicted by laboratory tests and actual full scale performance.
- confirmation of post treatment requirements (via pH adjustment, heavy metals removal, etc.).
- examination of corrosion coupons to evaluate potential construction materials for future commercial applications.
- evaluation of reactor heat-up time with both liquid and solid feeds.
- performance of mass balances on the process to define more accurately liquid loss during reaction.

FUTURE WORK

The batch reactor is best suited to relatively low flow, high concentration wastes. The other problem facing the plating industry is high flow, low concentration rinse waters. This is best treated in a continuous flow system. A planned extension of the present work is to design, construct and operate a continuous flow demonstration unit for the treatment of dilute cyanide wastes.

A continuous process flowsheet is given in Figure 5.

In future applications where a batch scale system is desired, the drum processing feature may not be required. In this case, loading and unloading of the reactor will be done by simple liquid transfer pumps.

Automation of the batch process would be a desirable feature for a liquid cyanide treatment system. An automated cycle for the operation of the batch system would be as follows:

- automatic loading of the reactor
- automatic heat-up to the selected operating temperature
- maintenance of the operating temperature and pressure for a specified period of time
- automatic reactor cooldown
- automatic discharge of the reactor contents
- automatic shut off.

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Renovation of Electroplating Rinse Waters with Coupled-Transport Membranes

W. C. Babcock, E. D. LaChapelle and R. W. Baker*

ABSTRACT

A new membrane process is described that can be used to recover plating chemicals from electroplating rinse waters. The process, called coupled transport, is based on liquid membranes that are comprised of a thin, polymeric microporous support containing a metal-ion complexing agent within the pores. Metal ions present in the rinse solutions are transported across these membranes and can be concentrated into a relatively small volume. The results of a small-scale field test are presented in which hollow-fiber coupled-transport membranes were used to recover chromium from chrome-plating rinse waters. The results of a 125-day test are used as the basis of an economic analysis that predicts a 1.7-year payback period for a full-sized coupled-transport unit.

INTRODUCTION: THE USE OF MEMBRANES IN THE TREATMENT OF ELECTROPLATING RINSE WATERS

Electroplating rinse waters are dilute solutions of plating chemicals that result from dragout of the chemicals from the plating bath into the rinse baths. The discharge of these rinse waters not only creates pollution problems, but also results in a loss of valuable chemicals. Current processes for treating the rinse waters involve precipitation of the toxic components (mostly metal ions) as a sludge. These sludges must then be disposed of in hazardous waste sites, where they remain as a threat to the environment. There is little doubt that in the future the favored processes for rinse water treatment will be those that permit recovery of the plating chemicals in a reusable or valuable form. Several membrane processes fall into this category.

The major composition of electroplating rinse waters are metal ions such as Ni^{++}, Cu^{++}, and $Cr_2O_7^{=}$. The ions can be recovered from the rinse solutions and concentrated using basically the two types of membrane separation processes shown in Figure 1. In the process in Figure 1a, a membrane is used that is permeable to water but impermeable to ions. Thus, when water flows through the membrane the rinse water becomes more concentrated in ions and reusable rinse is produced on the opposite side of the membrane. The only such process that has been used for treating electroplating rinse waters is reverse osmosis. In reverse osmosis, water is forced through the membrane by pressure on the upstream side—typically about 400 psi.

In the process shown in Figure 1b, the membrane is permeable to ions but impermeable to water. In this case, as ions permeate the membrane the rinse water becomes more dilute and a concentrated solution of ions is produced on the opposite side of the membrane. Several such processes are currently being considered for treating electroplating rinse waters. These include electrodialysis, for which the driving force to concentrate metal ions is derived from an electric field imposed across the membrane, and Donnan Dialysis and coupled transport, in which the energy for concentrating the metal ions is derived from the flow of other types of ions across the membrane.

Of the membrane processes with potential for treating electroplating rinse water, reverse osmosis is the most highly developed due to extensive research and development over the past 20 years to apply the process to water desalting. And, although reverse osmosis has been used to a limited extent in the electroplating industry, it has inherent drawbacks that may prevent its widespread use. Foremost

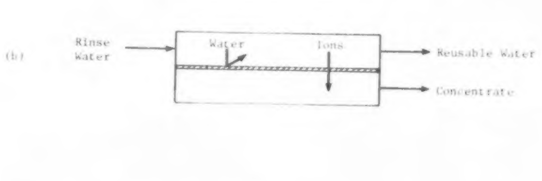

Fig. 1—Two Methods of Treating Electroplating Rinse Water with Membranes

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among these drawbacks is the fact that the membranes are readily fouled either by suspended matter in the rinse baths that is filtered out by the membrane or by dissolved components, such as metal hydroxides, that precipitate on the membrane as the rinse solution is concentrated. Fouling necessitates frequent membrane cleaning and shortens membrane lifetime, leading to high operating costs. A second limitation is that reverse-osmosis membranes are chemically degraded by solutions of extreme pH or oxidation-reduction potential, thus preventing their use with rinses from common plating operations such as acid copper or chrome.(1) Finally, reverse osmosis cannot in general be used to concentrate plating chemicals back to their concentrations in the plating bath because either 1) the osmotic pressure of the plating bath is higher than the operating pressure or 2) the membrane is not sufficiently selective for water over plating chemicals to produce reusable water when the rinse is concentrated to plating bath strength.(2)

Some of the limitations of reverse osmosis can be potentially overcome by coupled transport, which is a membrane process of the type shown in Figure 1b. For example, since there is no fluid flow through the membranes, fouling by filtration of suspended matter does not occur. Furthermore, since the process is not pressure-driven, the concentration of plating chemicals that is achievable is not limited by the osmotic pressure of the concentrate. Finally, coupled-transport membranes will withstand relatively harsh chemical environments such as those encountered in treating chrome-plating rinses.

COUPLED TRANSPORT

Description of the Process

Coupled transport membranes consist of an organic, liquid complexing agent held by capillarity within the pores of a microporous membrane. Metal ions are transported across the membrane as neutral complexes and can be "chemically pumped" from a dilute aqueous solution to a concentrated aqueous solution by the coupled flow of a second ionic species.

The process is illustrated in Figure 2, which shows coupled transport of dichromate ion and hydrogen ion with a tertiary amine (R_3N). On the left side of the membrane, designated as the feed side, dichromate ion plus hydrogen ions are extracted via the reversible reaction

$$2H^+_{(aq)} + Cr_2O_7^{=}{}_{(aq)} + 2R_3N_{(org)} \rightarrow (R_3NH)_2\,Cr_2O_7\,{}_{(org)} \cdot \quad (1)$$

Here, (aq) and (org) refer to species soluble only in the aqueous and organic phases, respectively. Extraction of dichromate ion is favored at the low pH of the feed solution. The amine-dichromate complex then diffuses to the opposite side of the membrane, designated as the product side. The pH of the product solution is high, leading to the reverse reaction in Equation 1. Chromic acid is released to the product solution and the free amine is regenerated. In the product solution, dichromate ion is converted to chromate ion via the reaction

$$2H_2O + 2OH^- + Cr_2O_7^{=} \rightarrow 2CrO_4^{=} + 3H_2O \cdot \quad (2)$$

The mechanism in Figure 2 leads to the flow of chromium from a dilute feed solution to a concentrated product solution as hydrogen ions flow from a feed solution of low pH to a product solution of high pH. This process can be used to remove chromium from chrome-plating rinse waters, where it is present as chromic acid, and to concentrate it into a small, easily manageable volume.

A similar process that can be used to concentrate cations such as copper ion is shown in Figure 3. In this case, complexing agents such as β-diketones and oximes (designated RH in the figure) carry the metal ion in one direction and hydrogen ions in the opposite direction. Metal cations are chemically pumped from a dilute feed solution to a concentrated product solution by the coupled flow of hydrogen ions in the opposite direction, from a solution of low pH to one of high pH. Processes such as that for dichromate ion, in which the ions flow in the same direction across the membrane, are called co-transport; those in which the ions flow in the opposite direction, such as with copper, are called counter-transport. Both processes have been studied extensively on a laboratory scale (3-10) but have not as yet been used in commercial applications.

Laboratory Demonstrations of the Process

To demonstrate the concepts of co- and counter-transport, the results of laboratory experiments with chromium and copper are presented. In these experiments coupled-transport membranes with 20 cm^2 of area were placed between the two compartments of permeation cells. These cells have been described in detail previously.(6) During an experiment, one compartment contained 100 ml of feed solution and the other compartment contained 100 ml of product solution. The coupled-transport membranes consisted of a microporous polypropylene membrane, Celgard 2400 (Celanese Plastics Co., Greer, South Carolina) impregnated with diluted complexing agent using methods described elsewhere.(6, 9)

The results of experiments with chromium are presented in

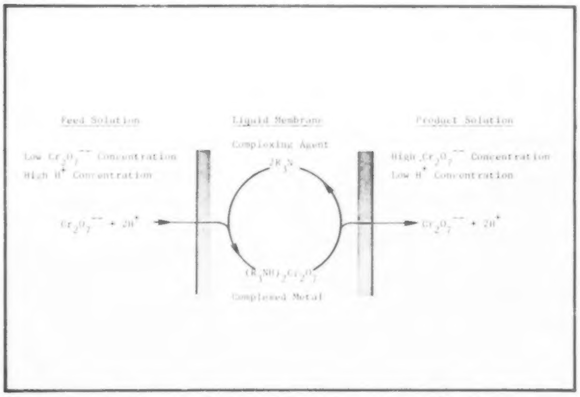

Fig. 2—Coupled Transport of Chromium Across a Liquid Membrane

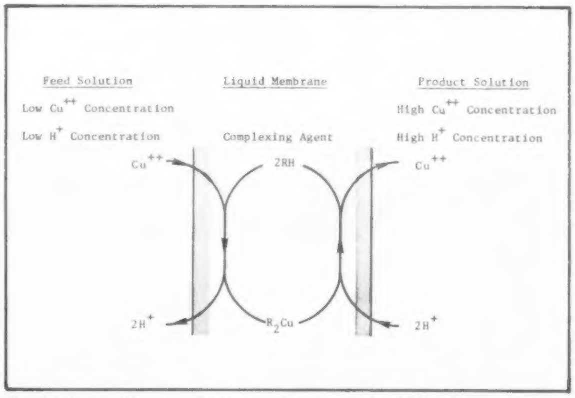

Fig. 3—Coupled Transport of Copper Across a Liquid Membrane

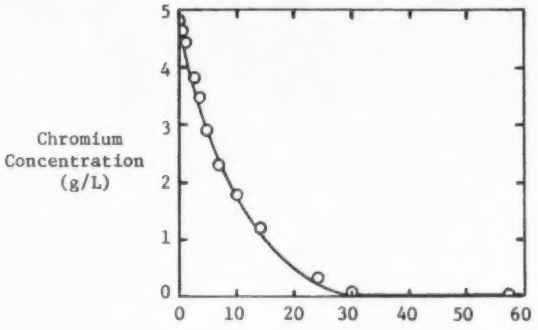

Fig. 4—Chromium Concentration in the Feed Solution as a Function of Time

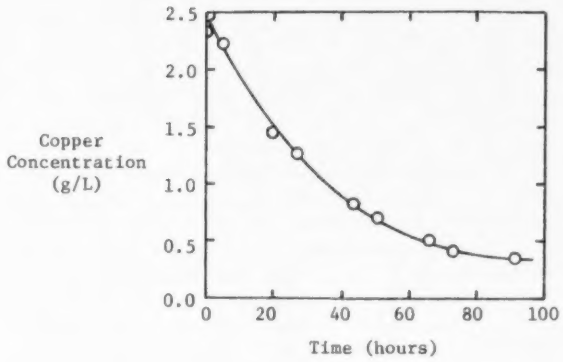

Fig. 5—Copper Concentration in the Feed Solution vs. Time

Figure 4, and those for copper are in Figure 5. These are plots of the metal-ion concentration in the feed solution vs. time. Because metal ions are transported out of the feed solution, the concentration decreased.

In the chromium experiment, metal ions were transported from the feed solution (initially 5 g/L) to a concentrated product solution. At the completion of the experiment, only 16 ppm chromium remained in the feed solution, with about 155,000 ppm in the product solution. This represents a concentration factor of 155,000/16 ≅ 9700. It should be noted that, from a practical standpoint, co-transport of chromium from a chrome-plating rinse solution would result in a concentrate of sodium chromate. Although this concentrate cannot be returned directly to the plating bath, it represents a valuable product that could be used in other metal-finishing processes such as cleaning or etching, or perhaps in other industries (e.g., for leather tanning).

In the experiment with copper, a synthetic acid-copper plating solution was used for the product solution. This solution was diluted by a factor of 40 to represent a rinse solution and was used for the feed. Copper was transported across the membrane from the feed to the product solution, indicating that counter-transport could be used to recover copper from rinse solutions by circulating the plating solution on the product side of the membrane. Thus, copper would be returned directly to the plating solution for reuse.

Process Scale-Up with Hollow-Fiber Modules

For practical applications of coupled-transport, the way in which the membranes are modularized will have a strong bearing on both the operation and economics of the process. One possible design would be a simple plate-and-frame module using the microporous polypropylene membranes used in our laboratory test cells. However, plate-and-frame units are unlikely to be the optimum membrane configuration for large-scale plants because of their relatively high cost per unit area. We believe that hollow-fiber membrane modules represent an economical module configuration, and we have developed hollow-fiber modules such as that shown in Figure 6.

The microporous fibers in these modules are made of polysulfone, a chemically resistant thermoplastic. A cross section of a typical fiber is shown in Figure 7. During module operation, feed solution flows through the fiber lumens and product solution flows along the outside of the fibers. The organic complexing agent is held in the porous fiber walls and metal ions are transported from the lumen to the outside of the fiber.

Field Tests on Chrome-Plating Rinse Water

Field tests were performed with a small hollow-fiber unit equipped with two modules having about 15 ft^2 of membrane area each. The tests were performed at a decorative chrome shop that utilizes a three-rinse counter-flow system, and the unit was installed to treat solution from the first rinse, as shown in Figure 8. In this configuration, coupled transport is used to maintain the concentration of the first rinse solution at a value that leads to adequate rinsing when

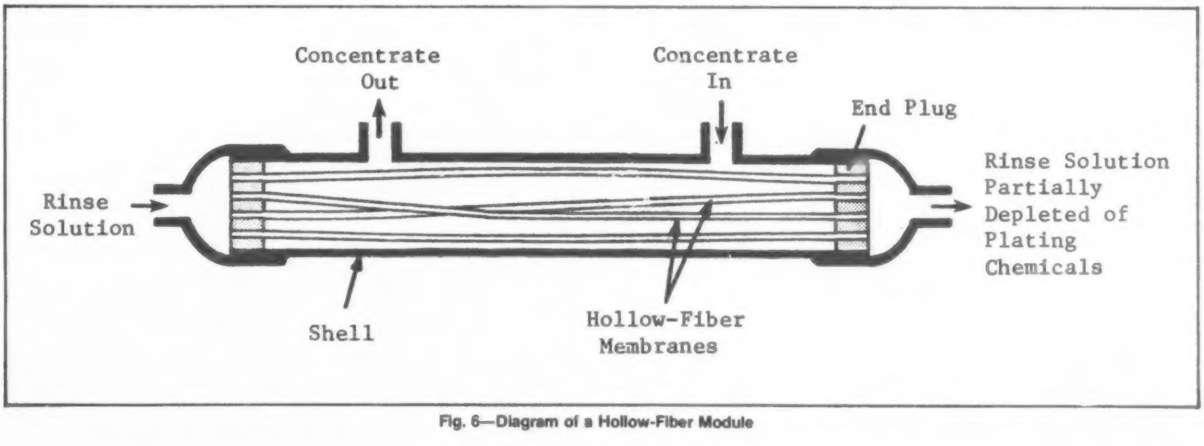

Fig. 6—Diagram of a Hollow-Fiber Module

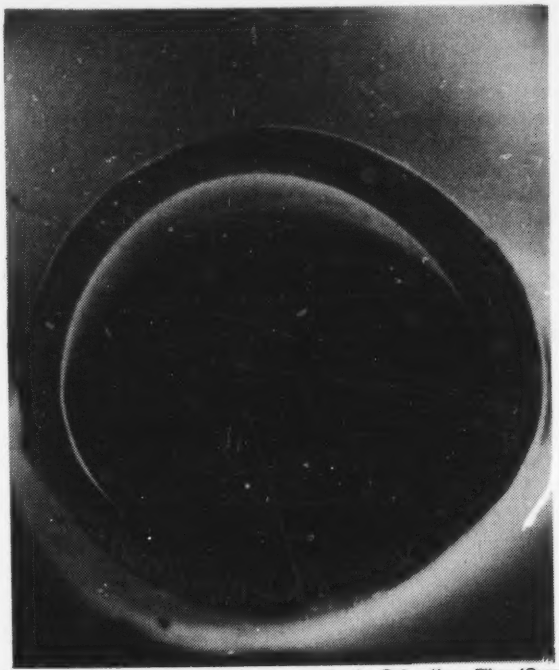

Fig. 7—Scanning Electron Photomicrograph of a Polysulfone Fiber (Cross Section)

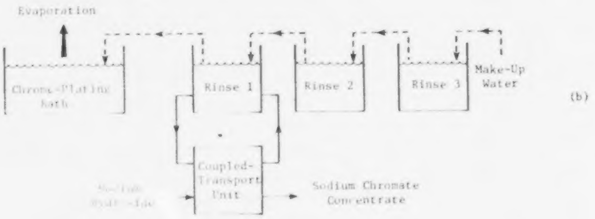

Fig. 8—Treatment of Chrome-Plating Rinse Water with Coupled Transport

Fig. 9—Hollow-Fiber Coupled-Transport Unit in Plating Shop

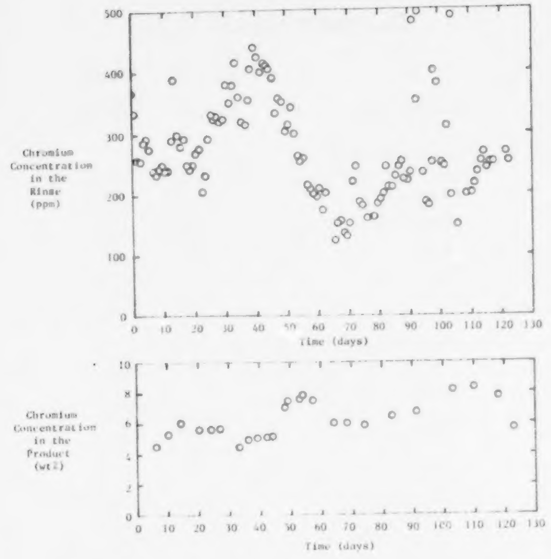

Fig. 10—Results of a Field Test Showing the Concentration of Chromium in the Rinse Solution and in the Sodium Chromate Concentrate vs Time

the counter-flow of rinse water is equal in volume to the evaporative loss from the plating bath. A photograph of the unit in the plating shop is shown in Figure 9.

The chromium concentration in the first rinse and in the sodium chromate concentrate produced by the coupled-transport unit are shown for a 125-day test in Figure 10. During this test, chromium was concentrated between 150- and 500-fold, with the concentrate containing on the average of about 6 wt% chromium.

In addition to monitoring the chromium concentrations, we also determined the chromium flux, which is the rate at which chromium is transported across the membranes. The flux of a permeant is a key factor in the economics of all membrane processes; in general, the higher the flux, the better the process economics. For the 125-day test in Figure 10, the flux was about 5 lb of chromium per square foot of membrane per year (5 lb/ft^2-year). A second test was also conducted with modified modules that yielded fluxes of about 20 lb/ft^2-year. However, performance of these modules deteriorated after only about 50 days of operation. We are currently engaged in further development of these high-flux modules to improve their long-term performance.

PROCESS ECONOMICS

Although coupled transport is still in the developmental stage, it can be shown that the process potentially offers extremely favorable economics compared with other chromium recovery technologies, such as distillation or ion exchange. The economic analysis presented here is modeled after a similar analysis performed by the EPA on distillation and ion-exchange units that recover approximately 5000 lb/year of chromium.[11] The objective of the analysis is to predict a payback time on invested capital for a treatment system based on 1) the value of the chromium recovered, and 2) the savings in the costs of chemical precipitation and disposal of the sludges that result from current methods of treating rinse waters.

For the purposes of comparing coupled transport with distillation and ion exchange, we have estimated the costs of coupled-transport units that will recover 5000 lb/year of chromium. As shown in Table I, two units were considered: one with 1000 ft^2 of membrane area and one with 250 ft^2 of membrane area. The larger unit would be required with

Table 1
Economics of Two 5000-lb/year Coupled-Transport Units

Unit Size	1000 ft²	250 ft²
Installed Cost	**$10,000**	**$4,500**
Annual Operating Costs		
Depreciation (20%)	2,000	900
Chemicals	2,000	2,000
Module replacement	1,500	400
Labor	700	700
	6,200	4,000
Annual Savings		
Chromium recovered as Na_2CrO_4(~16,000 lb/yr)	4,000	4,000
Savings in precipitation & sludge disposal	9,000	9,000
	13,000	13,000
Net Savings = Annual Savings - Operating Costs	6,800	9,000
Net Savings After Tax (46% Bracket)	3,700	4,900
Cash Flow from Investment = Net Savings After Tax + Depreciation	5,700	5,800
Payback period = $\frac{\text{Total Investment}}{\text{Cash Flow}}$	1.7 years	0.8 years

chromium fluxes of 5 lb/ft^2-year, which is the flux we obtained with our most reliable modules; the smaller unit could be used if the modules that yield fluxes of 20 lb/ft^2-year are developed further.

The installed costs of these units are estimates based on the manufacturing costs of several hollow-fiber units we have constructed plus approximately a 40% mark-up to cover marketing distribution, and profit. The major annual operating costs are depreciation, chemicals, module replacement, and labor. The only chemical cost for the process results from use of sodium hydroxide in the conversion of chromic acid to sodium chromate. To recover 5000 pounds of chromium, approximately 8000 pounds of sodium hydroxide are required and bulk prices of sodium hydroxide are about $0.25/lb.(12) For module replacement costs we have assumed a lifetime of 2 years and a module cost of $3.00/ft^2 of membrane. Again, module costs are based on our estimated manufacturing costs plus a mark-up. A 2-year lifetime is assumed to be possible based on long-term laboratory tests with the lower-flux modules that have currently run 500 days. Labor costs are expected to be low, and as a rough guide we have used the same labor costs as those for similarly sized distillation and ion-exchange units.(11)

Because the sodium chromate cannot be returned directly to the plating bath and may need further processing and shipping, we have taken a credit of only $0.25/lb, which is less than half the current bulk price of $0.55/lb.(12) For the annual savings in precipitation and sludge disposal costs we have used the same savings as used in the EPA analysis of distillation and ion exchange: ~$1.80/lb of chromium recovered.(11)

The estimated payback periods are short for both unit sizes, with the smaller unit having a payback period of less than one-half that of the larger. This shows the incentive to develop high-flux modules. The calculated payback periods for similarly sized distillation and ion-exchange units are 7.9 years and 5.2 years, repectively,(11) showing that, if fully developed, coupled transport would offer an economical alternative to these processes.

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The Application of Donnan Dialysis To Electroplating Washwater Treatment

EPA/AES Research Project 60

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Abstract

The operation of a Donnan dialyzer as a means of removal of ionic contaminants from electroplating washwaters is discussed. The application of both anion-exchange and cation-exchange membranes for treatment of waste streams from various metal plating lines is considered. The on-going development of a field prototype Donnan dialyzer for removal of complex metal-cyanide anions from cyanide bath process washwaters is discussed.

DISCUSSION

Ion-exchange resins are of utility in separation processes because they can be used to remove ions from dilute electrolyte solutions. When contacted with a stripping solution of the proper concentation, the resins release the ions. If ion-exchange resins are in membrane form, they can be in contact with the dilute electrolyte solution and the stripping solution simultaneously, and the ion-exchange process can be continuous rather than cyclic. This ion-exchange membrane process is based on the Donnan equilibrium principle (1) and requires no electrical current or high pressure for operations, as would be required for electrodialysis or reverse osmosis. This process was first called Donnan dialysis by Wallace (2).

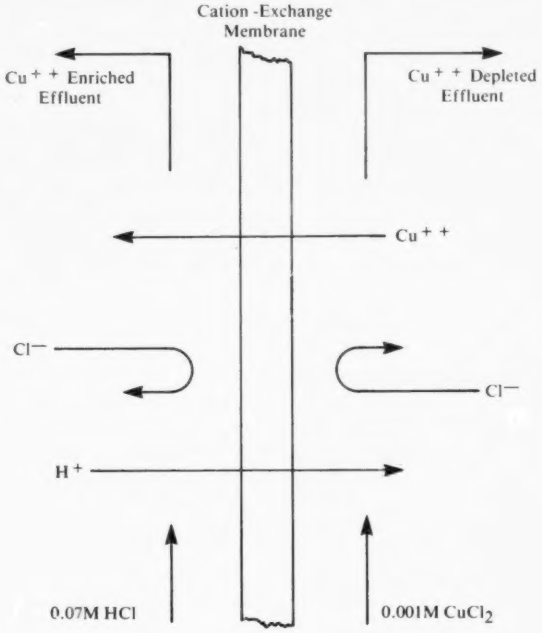

Fig. 1—Mechanism of Donnan Dialysis.

If solutions of two electrolytes are separated by a cation-exchange membrane, the anion composition of the two solutions must remain constant since the membrane is impermeable to anions. The cations, however, will redistribute between the two solutions until equilibrium is reached. This is shown in Figure 1, where the two solutions are 0.07M HCl and 0.001M $CuCl_2$, respectively. Due to the high concentration of HCl relative to the concentration of $CuCl_2$, there is an immediate flow of hydrogen ion across the membrane. Because the chloride ion cannot cross the membrane, there is a resultant loss of electroneutrality in the acid solution, and a charge potential builds across the membrane which is opposite in direction to the concentration potential gradient. This charge potential provides the driving force to transfer cupric ions from the feed across the membrane into the stripping solution. This process continues until the system comes to equilibrium. Donnan (1) showed that this equilibrium could be described by the generalized equation shown in Figure 2. By

$$\left[\frac{(C_i^{+Z})_l}{(C_i^{+Z})_r}\right]^{\frac{1}{Z}} = K$$

for any mobile cation i of valence Z, where K is the same constant for all cations in the system.

Fig. 2—Donnan Equilibrium Equation.

$$\frac{[H^+]_l}{[H^+]_r} = \left[\frac{[Cu^{++}]_l}{[Cu^{++}]_r}\right]^{\frac{1}{Z}}$$

Fig. 3—Donnan Equilibrium Conditions.

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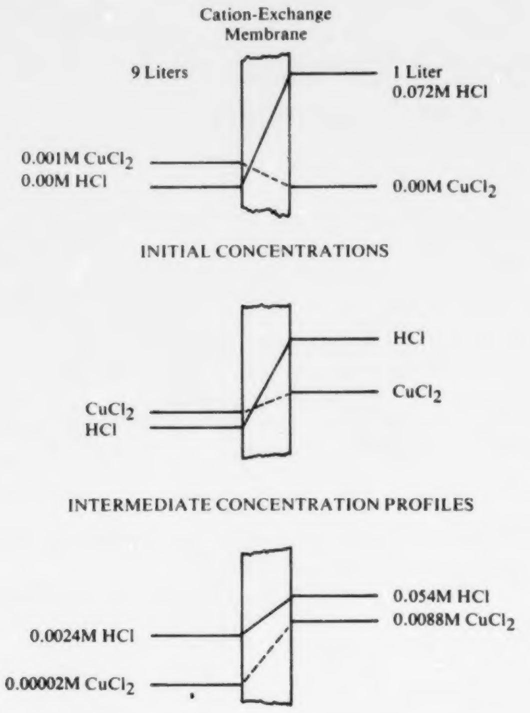
application of this equation to the present example, the equilibrium conditions can then be described by the equality shown in Figure 3.

For a system in which the volume ratio of feed to stripping solution is nine, the initial and calculated final equilibrium concentrations are shown in Figure 4. Ninety-eight percent of the cupric ion would be transferred across the membrane, and the copper in the stripping solution would be concentrated by a factor of 8.8 compared to the initial feed concentration.

Southwest Research Institute became interested in Donnan dialysis about five years ago as a result of a continuing research program on preparation of permselective membranes by radiation initiated graft polymerization. By using this preparative technique, we were able to prepare both anion- and cation-exchange membranes having controlled levels of ion-exchange capacity and hydrophilicity.

Initial studies to evaluate the performance of such membranes in Donnan dialysis were conducted in an in-house research program (3). A simple dialysis system consisting of a flat membrane, thin channel dialysis cell, two recirculation pumps, and two reservoirs was used in these initial evaluations. The feed and stripping solutions were circulated through the system and samples of each solution were periodically taken and analyzed for the metal of interest. The results obtained using a strong acid ion-exchange membrane to remove various metal cations from an aqueous feed stream are shown in Figure 5. As can be seen, very high percentage removal was obtained for all six metal cations, and the cations were concentrated approximately twentyfold in the stripping solution. Examination of the data also indicated that the rate of metal ion removal was proportional to the metal ion concentration in the absence of boundary layer effects which were minimized by high solution flow velocities through the thin channel cell halves. The rate of metal removal was found to follow a first order rate equation, allowing calculation of a metal removal rate constant as shown in Figure 6.

Since some metals are electroplated from cyanide baths, a series of experiments were also conducted in which removal of metals as their complex cyanide anions was accomplished using a strong base anion-exchange membrane. The results of these experiments are shown in Figure 7. As was the case with the metal cations, high percentage removal of all four



INITIAL CONCENTRATIONS

INTERMEDIATE CONCENTRATION PROFILES

EQUILIBRIUM CONCENTRATIONS

Fig. 4—Removal of CuCl$_2$ from a Dilute Solution by Donnan Dialysis.

$$k = \frac{\ln\left(\frac{C_o}{C_t}\right)}{t}$$

where C_o - initial concentration
C_t - concentration at time t
t - time, min
k - rate constant, min^{-1}

Fig. 6—Metal Removal Rate Constant.

Figure 5
Removal of Metal Cations from Water Via Donnan Dialysis

Metal Ion	*Feed conc., ppm Initial*	*Final*	*% Removal*	*Rate Constant, Metal Removal min^{-1}*	*Concentration* Factor*
Cd^{++}	34.2	0.1	99.7	6.3	18.9
Cu^{++}	27.3	<0.05	100.0	6.5	19.8
Ni^{++}	34.6	0.1	99.7	5.5	18.1
Zn^{++}	32.3	0.1	99.2	5.6	19.4
Mg^{++}	12.2	0.1	99.2	5.6	19.4
Fe^{++}	46.5	0.2	99.6	5.4	18.3

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* Final conentraiton in stripping solution/initial concentration in feed membrane: polyethylene-g (polystyrene-co-divinyl benzene) sulfonic acid

Cell Parameters:
Feed Volume 6 liters
Stripping Solution Volume 0.3 liters, 0.57N NaCl
Recirculation Flow Rate 425 mL/min
Run Duration 4 hours

Figure 7
Removal of Metal-Cyanide Complex Anions from Water Via Donnan Dialysis

Metal Ion	*Feed conc., ppm* *Initial*	*Final*	*% Removal*	*Rate Constant, Metal Removal min-1*	*Concentration* Factor*
Ag	50.2	0.3	99.4	4.8	16.8
Cu	48.2	0.2	99.6	3.8	17.9
Cd	51.3	0.1	99.8	4.1	18.2
Zn	46.4	0.3	99.4	3.7	17.4

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* Final concentration in stripping solution initial concentration in feed membrane: polyethylene-g[poly (N-methyl-4-vinylpyridinium chloride)]

Cell Parameters:		
	Feed Volume	6 liters
	Stripping Solution Volume	0.3 liters, 0.5N NaCl
	Recirculation Flow Rate	425 mL/min
	Run Duration	4 hours

Figure 8
Effect of Metal Ion Concentration on Ion Transport

Membrane	*Metal Ion Transport Rate, min⁻¹* *Low Concentration** *Cu*	*Cd*	*Zn*	*High Concentration*** *Cu*	*Cd*	*Zn*
E11Q4	3.1	2.8	1.9	1.5	1.5	1.5
E12Q4	2.3	2.2	2.9	0.7	0.8	0.6
E16Q1	2.5	1.6	0.7	0.6	0.9	—†
E18Q1	2.2	1.4	0.6	1.41	0.6	0.4

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* Nominal 50 ppm in metal ion.
** Nominal 500 ppm in metal ion.
† Membrane ruptured.

Figure 9
Properties of High Transport Rate Membranes

Membrane number	*Membrane Type*	*Equilibrium Water Content g H_2O/g*	*Ion-Exchange Capacity meq/dry g*
E11Q4	$(4\text{-VP})CH_3I$	1.08	2.5
E12Q4	$(4\text{-VP}/N\text{-VP})CH_3I$	2.45	2.6
E16Q1	$(VCB)(CH_3)_3N$	1.52	2.2
E18Q1	$(VBC/N\text{-VP})(CH_3)_3H$	1.00	2.2

metal-cyanide complex anions was obtained. It can be seen that the rate constants for metal removal are somewhat lower for this anion-exchange membrane than those observed for the cation-exchange membrane. This is primarily due to the lower ion-exchange capacity of the anion membrane (1.8 meq/g) compared to the capacity of the cation membrane (2.3 meq/g).

Subsequent to this in-house research, a program was conducted with the Industrial Environmental Research Laboratory, Environmental Protection Agency, Cincinnati, Ohio, for the development of improved membranes for Donnan dialysis. The objective of this program was aimed at developing anion-exchange membranes for the removal of

Figure 10
Replicate Evaluations of Membrane E11Q4

Membranes†	*Metal Ion Transport Rate, min⁻¹* *Low Concentration** *Cu*	*Cd*	*Zn*	*High Concentration*** *Cu*	*Cd*	*Zn*
E11Q4‡	3.1	2.8	1.9	1.5	1.5	1.5
E11Q4-B	3.4	3.1	2.0	1.5	1.3	1.3
E11Q4-C	3.2	2.7	2.1	1.6	1.4	1.3

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*Nominal 50 ppm in metal ion.
**Nominal 500 ppm in metal ion.
†Separate sets of membranes—same grafting run, separate quaternization reaction.
‡From Figure 8.

metal-cyanide complex anions from electroplating process washwaters.

The emphasis was placed on anion membranes due to two reasons. First, there are available cationic membranes developed for other purposes (electrodialysis, chlorine-caustic electrololytic membrane cells) which have the requisite mechanical and chemical properties to provide good performance in Donnan dialysis for cation removal. Eisenman (4) has reported on both laboratory and field evaluation of Donnan dialysis for the recovery of nickel from the rinse water on a Watts-type nickel plating line. This work utilized modular tube and shell-type dialyzers with each module containing about 380 tubes (0.025 in ID) to provide 20 ft^2 of membrane area. The dialysis system, containing six modules with a total of 120 ft^2 membrane area, was capable of nickel removal rates of 2 $g/hr/ft^2$ when operated with 1 to 2 normal acid strip.

Secondly, the available anion-exchange membranes have lower ion-exchange properties and are prone to fouling, making them less useful for Donnan dialysis.

During this program, membranes were prepared by grafting polyethylene basestock (1 mil thickness) with either 2-vinylpyridine, 4-vinylpyridine, or vinylbenzyl chloride. After grafting, the membranes were quaternized. The vinylpyridine-grafted films were quaternized with alkyl halides; the vinylbenzyl chloride-grafted films were quaternized with trialkyl amines. The degree of grafting (and ultimately the ion-exchange capacity) was varied by using different concentrations of monomer in the grafting reaction. The hydrophilicity of the membranes was varied by use of different alkylating reagents.

The membrane test system was modified to increase the membrane area and to operate with single pass feed solution and stripping solution recirculation. All preliminary membrane evaluations were conducted with feed consisting of electroplating bath solutions diluted to give metal ion concentrations of nominal 50 ppm. All membranes were evaluated using feeds containing copper, cadmium, or zinc as their cyanide complex anions. The initial evaluation indicated that the ion transport rates across the membrane are proportional to the ion-exchange capacity, i.e., the higher the ion-exchange capacity, the higher the transport rate. It was also found that membrane hydrophilicity plays an important role in ion transport. Membranes of low hydrophilicity which imbided only small amounts of water had low to zero ion transport rates regardless of ion-exchange capacity. Ion transport rates increased with increasing hydrophilicity up to a point and then decreased. If a membrane absorbs large volumes of water, the charge density within the membrane is decreased due to the large wet volume of the membrane, and there is a loss of ion selectivity. The decreased fixed charge density leads to less rejection of cations; cation leakage across the membrane leads to decreased Donnan potential across the membrane and results in reduced ion transport rates.

Four membranes were selected for more extensive evaluation. Two membranes were based on 4-vinylpyridine and two on vinylbenzyl chloride-grafted films. These membranes were evaluated at metal feed concentrations of nominal 50 ppm and nominal 500 ppm for all three metals of interest. The results are shown in Figure 8. All four membranes showed reasonable transport rates at 50 ppm feed. There is a reduction in rate for all membranes on going to 500 ppm feed. This is primarily due to change in the feed concentration to stripping solution concentration ratio which led to a lower driving force for ion transport. To have maintained the same ratio with the 500 ppm feed as was used with the 50 ppm feed would have required 2.0 normal NaCl stripping solution. For these anion-exchange membranes, that concentration of stripping solution would lead to excessive chloride ion leakage and very low transport rates. The two membranes E12Q4 and E16Q1, which showed the poorest performance at the high level feed, are the more hydrophilic of the four, as shown in Figure 9. Membrane E11Q4 showed the best overall performance, indicating the best balance of ion-exchange capacity and hydrophilicity.

Replicate studies of membrane E11Q4 were conducted using three different sets of membranes. The membranes were prepared using material from the same grafting run but which were quaternized in separate batches. Metal ion transport rates for all three sets of membranes for all three metals at both low and high metal ion concentrations were made, with the results shown in Figure 10. These results showed that uniform grafting and quaternization can be obtained in the membrane preparation, as indicated by the uniformity of the rate constants obtained.

Based upon these results, a field evaluation of a prototype Donnan dialyzer is currently in the planning stages. These plans call for preparation of sufficient quantities of membrane E11Q4 (400 to 800 ft^2) to construct a prototype plate and frame dialyzer. Calculations based upon the above data indicate that this unit should give $> 95\%$ removal of electroplating washwaters containing nominal 500 ppm levels of copper, cadmium, or zinc at feed flow rates of 3 to 5 gpm.

This dialyzer will be operated on washwaters in commercial electroplating shops to provide engineering data on membrane performance and on long-term stability of the membranes under actual use conditions. The field data obtained should also allow assessment of the cost effectiveness of Donnan dialysis as a means of controlling effluent emissions levels in electroplating process wastewater discharges.

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This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

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